University of Alberta Library
0 1620 3069200 6

For Reference

NOT TO BE TAKEN FROM THIS ROOM

THE DETERMINATION OF SELENIUM IN SOILS AND PLANTS.

THE DETERMINATION OF FLUORIDES, SULFATES, AND IRON IN ALBERTA WATERS.

by

Michael Rossi, B.Sc.

University of Alberta,
Edmonton, Alberta.

April, 1940.

Ex libris
universitatis
albertaensis

Digitized by the Internet Archive
in 2018 with funding from
University of Alberta Libraries

https://archive.org/details/determinationofs00ross

Thesis
1940
#18

THESIS

THE DETERMINATION OF SELENIUM IN SOILS AND PLANTS.

THE DETERMINATION OF FLUORIDES, SULFATES, AND IRON IN ALBERTA WATERS.

Submitted in partial fulfilment of the requirements for the degree of Master of Science.

by

Michael Rossi, B.Sc.
Under the direction of Dr. O.J. Walker
In the Department of Chemistry.

Time devoted to thesis work was 5.3 out of 7.0 months or three full courses, counting four courses as one academic year's work.

Edmonton, Alberta. April, 1940.

Table of Contents

Page
Acknowledgement---------- 1A

Section 1 - The Determination of Selenium in Soils and Plants.

Introduction---------- 1
Experimental Method---------- 5
Results---------- 9
Discussion of Results---------- 12
Summary---------- 13
References---------- 14

Section 2 - Further Study on Occurrence of Fluorides in Alberta Waters.

Introduction---------- 15
Experimental Method---------- 16
Results---------- 20
Summary---------- 23
References---------- 24

Section 3 - Determination of Sulfates in Alberta Waters

Introduction---------- 25
Purpose of this Investigation---------- 31
Discussion of Methods of Analysis---------- 31
Introduction to Analytical Determination of Sulfates---------- 42
Analytical Procedure---------- 45
Results---------- 49
Discussion of Results---------- 59
Summary---------- 63
References---------- 65

Section 4 - Determination of Iron in Alberta Waters

Introduction---------- 74
Analytical Methods---------- 76
Results and Discussion---------- 79
Comments---------- 83
Summary---------- 84
References---------- 85

ACKNOWLEDGEMENT

The writer wishes to express his sincere appreciation and gratitude to Dr. O.J. Walker for his helpful advice and criticism during the carrying out of this investigation.

Grateful acknowledgement is made to Mr. J.M. MacGregor, formerly with the Department of Agriculture, for the collection of the soil and plant samples.

Grateful acknowledgement is made to the Provincial Laboratory for their cooperation in supplying the water samples.

DETERMINATION OF SELENIUM IN SOILS AND PLANTS

INTRODUCTION

Selenium has been found in soils derived from Cretaceous shales (1) and also soils of pre- and post-Cretaceous formations. Large areas in the provinces of Alberta and Saskatchewan are of these geological formations. According to Byers (2) selenium may be expected to be present in all soils derived from pyritiferous parent material. This is usually true provided, of course, that the selenium had not been washed away by percolating waters.

Selenium has been found present in soils in various forms. Previous work done by Byers and Williams (5) showed that selenium is apparently always present in iron pyrites. It appears to be always present in shales of the upper Cretaceous period and particularly in the lower portion of the Pierre and the upper portion of the Niobrara formations (2). The plains of Southern Alberta consists of the Belly River series and the overlying Bearpaw shale which constitutes all the strata of Pierre age. These geological beds are similar to the adjacent areas in Montana which are also of Pierre age (11) Pyritic nodules have been found in these formations. It may, therefore, be inferred that one of the forms in

which selenium is found in soils is as pyrites carrying selenium as a partial substitute for sulphur. Since selenium is present in pyrites it will not be available as a plant food or poison and this fact is relatively unimportant except as a possible source of selenium. Marcasite being susceptible to more rapid weathering may release selenium in soluble form (5). Selenium may also be present in soils as exceedingly insoluble basic ferric selenites, the approximate composition being $Fe_2 (OH)_4 SeO_3$ (4) and the soils containing water - soluble selenium may have it present in the form of selenates, possibly as calcium selenate ($Ca SeO_4$), which is readily available to plants.

Byers (3) has found that selenium is associated with soils occurring within narrow rainfall belts, that is, in regions with an annual rainfall of twenty inches or less. Under heavy rainfall, soluble selenium compounds are leached out of the soil and carried away in the drainage waters. Well irrigated areas with proper drainage provides an excellent means of decreasing the selenium content of the soils.

Vegetations growing on the types of soil described have been rendered toxic (2) due to the fact that selenium is absorbed by the plant. All plants do not absorb selenium and certain plants take it up in greater quantities than others growing in the same area. Two

species of Astragalus (1), A. pectinatus commonly known as narrow leaf milk vetch and A. bisulcatus or two-groved milk vetch, serve as "indicators" of seleniferous areas. Other plants which are toxic are wild aster, Russian thistle, western wheat grass, lambs-quarters, young wheat, and salt sage (3). According to Byers (2) the amount of selenium absorbed from seleniferous soils by plants is apparently dependent on (1) the quantity of selenium and its distribution in the soil profile (there exists no quantitative relationship between the soil content of selenium and the amount of selenium absorbed by the plant); (2) the kind of plant; (3) the portion of plant examined; (4) the seasonal variation in rainfall; (5) the soil composition, especially its available sulphur content. This last factor is the result of the findings of A. M. Hurd-Karrer (6). She has shown that since sulphur is chemically related to selenium, it is absorbed by plants when the ratio of selenium to sulphur is 1 to 12 or less in preference to selenium. Sulphur is an essential and necessary element in plant and animal tissue. But results of her work are not applicable under conditions which exist in toxic areas since seleniferous areas are in general already saturated with sulphur in the form of gypsum (7).

The distribution of selenium in soils and its content in plants is a world wide problem and an economic "set-

back." Livestock feeding on toxic vegetation are poisoned by the selenium (7). Selenium poisoning is divided into two general classes, the chronic type, "alkali disease" and the acute type, "blind staggers."

"Blind staggers," the severe type of poisoning, is the result of eating food containing large amounts of selenium. In the first stages there is a slight impairment of vision. In the next stage there is a more pronounced blindness accompanied by a depraved appetite. The last stage is characterized by various degrees of paralysis which usually results in death.

The symptoms of "alkali disease" are developed on eating a diet relatively low in selenium over a fairly long period of time. The mildest form of poisoning is retardation in rate of growth. Advanced stages of the disease are shown by loss of appetite, loss of hair, and soreness of the feet caused by a gradual separation of the wall of the hoof.

Selenized plants are eaten by stock only during a season of great drought. Under normal conditions of feeding, the animal will avoid all such plants since they possess an odor similar to rotten eggs (3).

Byers (3) states that any soil containing o.5p.p.m. and any vegetation containing 5 p.p.m. is potentially dangerous depending on what percent of the total diet is seleniferous.

Experimental Method

This work on the selenium content of soils and plants is a continuation of the survey made by W.E. Harris (8) in this laboratory on the selenium content of wheat and soils. The method is similar to that adopted by him. This method is that of Robinson (9) with the modifications suggested by Curl and Osborn (10).

The material was ground as finely as possible. 10 grams of the sample were placed in a round bottomed flask to which was added about half a gram of mercuric oxide as a catalyst, 50 c.c. concentrated sulphuric acid along with 12.5 c.c. concentrated nitric acid per gram of sample. The flask was placed in a fume cupboard under funnels with extended arms so that the fumes could be readily drawn off. After standing for about a half hour it was heated until the nitric oxide and the nitric acid were driven off and the solution turned dark in color.

After cooling the solution, it was distilled over with 40% hydrobromic acid and bromine. The distillation apparatus is the same as that devised by Robinson (9) as shown in Fig. I. Only ground glass joints could be used since corks and rubber stoppers are readily attacked by the hydrobromic acid and bromine. To the digest was added 100 c.c. of hydrobromic acid and about 2 c.c. of bromine. Distillation was continued until about 75 c.c.

of distillate had been collected, care being taken that a small amount of bromine comes over with the first few c.c.'s of solution.

Since much difficulty was encountered due to bumping, especially with soil samples, it was found necessary to add porcelain chips prior to the digestion stage. During distillation the heating was directed more towards the side of the flask rather than the center. These precautions greatly minimized the bumping and speeded up the digestion and distillation stages as greater heat could be applied.

In Fig. I, A is a 500 c.c. round bottom flask in which both the digestion and distillation were carried out.

At B are ground glass joints which connect the distilling flask to the adapter and the adapter to the condenser.

C is a thistle tube through which the hydrobromic acid and bromine may be added.

D are glass hooks which aid in holding the ground joints together by means of rubber bands.

E is a 200 c.c. erlenmeyer flask in which the distillate is received.

Selenium to be distilled over quantitatively must be in its tetravalent state. Hydrobromic acid causes the selenium to distil over almost completely in its

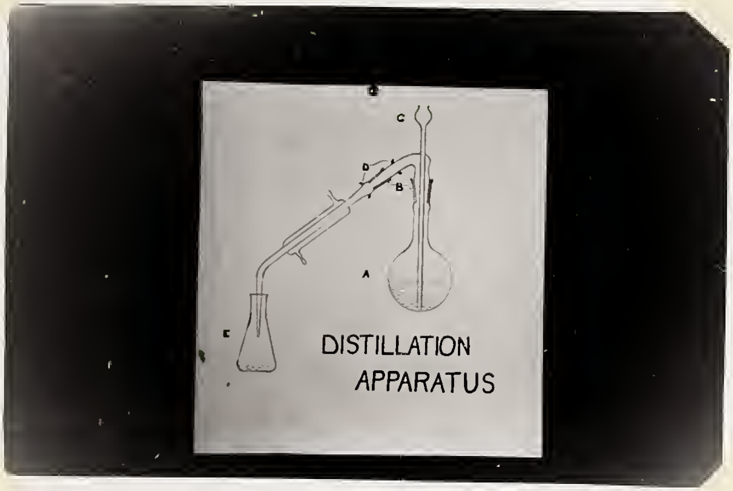


Fig. I

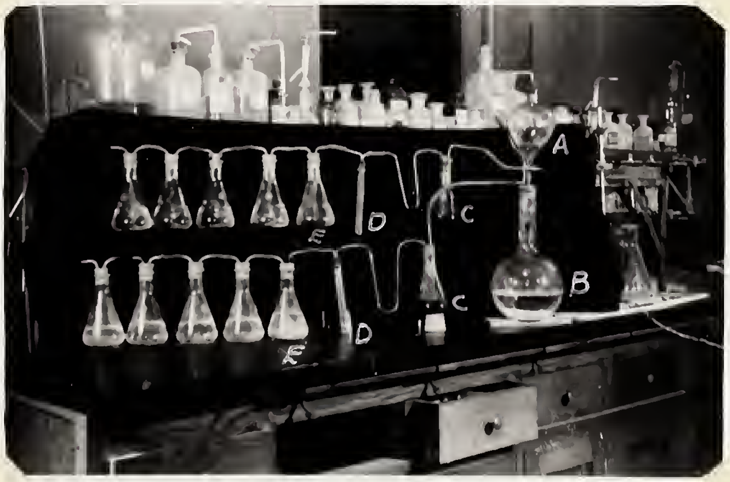


Fig. II

lower valence state, even when originally present in the higher valence state (12). The mixture is made strongly oxidizing by the addition of liquid bromine. The bromine serves to dissolve most of the metals and sulfides that are not attacked by hydrobromic acid and perhaps oxidize any remaining organic material. The excess bromine distills over and then the hydrobromic acid causes the selenium to be distilled as $Se\ Br_4$.

The selenium was next precipitated quantitatively from the distillate and other elements present by the reducing agent, sulphur dioxide.

$$Se\ Br_4 + 2SO_2 + 4H_2O \rightarrow 2H_2SO_4 + 4H\ Br + Se\downarrow$$

The sulphur dioxide to precipitate the selenium and reduce the bromine was produced by a simple apparatus shown in Fig II. Sulphuric acid in funnel A was dropped into a flask B containing a sodium sulfite suspension. The gas was dried by concentrated sulphuric acid in C and then passed through the solution D containing selenium. The excess sulphur dioxide was absorbed by the train of 5 flasks containing sodium hydroxide.

After passing an excess of sulphur dioxide through the solution, about 0.25 grams of hydroxylamine hydrochloride was added to ensure complete precipitation of the selenium. The flask was loosely stoppered and allowed to stand overnight.

The precipitated selenium was collected on an

asbestos mat in a gooch crucible and washed slightly with dilute hydrobromic acid containing hydroxylamine hydrochloride. The selenium was redissolved on the filter by means of 10c.c. of dilute hydrochloric acid saturated with bromine added in small portions, the solution being received in an 18mm. test tube. It was then reprecipitated in the colloidal condition with sulphur dioxide and hydroxylamine hydrochloride as in the earlier part of the experiment. The depth of the color produced by the precipitated selenium was compared in about four hours with standards precipitated in the same manner containing 0.000; 0.003; 0.006; 0.009; 0.012; 0.015; 0.02; 0.03 mg. of selenium in similar 10 c.c. volumes. A stock solution of selenic acid was prepared containing 1 mg. of selenium per c.c. For the purpose of making standards, a standard solution was made from this by diluting 10 c.c. of the stock solution to 1 litre.

The comparison of colors was best carried out on a white surface. Artificial light is unsatisfactory.

In the case of plants the concentration of selenium was too high to determine the content by the above procedure. After reprecipitation as above it was refiltered through a previously weighed gooch crucible, dried in an electric oven at 110°C. for one hour, cooled and weighed.

Results

The determinations of selenium were carried out on soils and on plants which grew on these soils to determine what relationship, if any, existed between the selenium content of the soil and the selenium content of the plant which grew on it. The results of the analysis of soils for selenium are shown in Table I. The results are tabulated according to the location from which they came, the geological formation over which they lie, and the depths of soil from which the samples were taken. The results of the analysis of plants are shown in the same table opposite to the corresponding soil profile on which they grew. The tabulation shows the part of the plant analyzed. The contents are expressed as parts of selenium per million parts of sample i.e. ppm.

These soils are of the Upper Cretaceous period. Three profiles were taken from the Bear Paw formation. Profile II was from the valley at the headwaters of Manyberries Creek; profile I near the same stream but approximately ten miles further down the creek, was taken from the Belly River formation. Profiles III and IV, both from the Bear Paw formation, were collected on the Dominion Range Experimental Station at Manyberries near an old dam about one mile south of the station

buildings. These formations correspond to the Pierre shales of Northern Montana adjacent to the southern plains of Alberta. The Pierre shales are noted for their selenium content and for rendering toxic the vegetations growing on them. The soil and plant samples were collected the latter part of July 1939, approximately one week after the disappearance of the blossoms on the plants.

Table I

Analysis of Soil and Plant Samples

	Profile	Location	Formation	Depth	Plant Portion	Se PPM.
Soil	I	N.E. 12-5-6-4	Belly-River	0-12"		0.5
				12-24"		0.4
				24-36"		0.35
				36-48"		0.4
Plant					Roots	0.3
Astragalus bisulcatus					Stalks	3.0
					Leaves	5.0
Soil	II	S.W. 34-6-5-4	Bear-Paw	0-12"		0.3
				12-24"		0.4
				24-36"		0.3
				36-48"		0.5
Astragalus bisulcatus					Roots	360.
					Stalks	465.
					# Leaves	170.
Soil	III	N.W. 10-2-4-4	Bear-Paw	0-12"		0.7
				12-24"		0.3
				24-36"		0.3
				36-48"		0.4
Astragalus pectinatus					Stalks	30.
					Leaves	120.
Astragalus bisulcatus					Roots	220.
					Stalks	200.
					Leaves	600.
Soil	# IV			0-12"		0.4

#profile IV taken twenty feet south of the others on the same location.

Value of leaves from profile II low because it was difficult to remove the soil from this particular sample.

Discussion of Results

Thirteen samples of soil have been analyzed for selenium. The values found varied from 0.3 to 0.7 PPM. The results show that there is no quantitative relationship between the depth of the soil and its selenium content. Byers (2) stated that the distribution of selenium in soils is not uniform in any area examined, either in the surface soils or in the soil profile.

The roots, stalks, and leaves of four plants were examined. The values found were 0.3 for the roots to 600 PPM for the leaves. Byers also found that there exists no quantitative relationship between the amount of selenium in soil and the amount of selenium in the plant grown on this soil. The concentration of selenium varies for different parts of the plant. The greatest concentration has been found in the leaves with the least amount in the roots. Byers was able to analyze the flowers in which he found the greatest concentration. He also found the least in the roots.

Summary

The method used for the selenium determination was that adopted by W. E. Harris (8). This has been described in detail.

The soils and plants that were analyzed for selenium may be considered as potentially dangerous. Large areas of Alberta are of the Pierre series, especially the southern plains lying adjacent to the Pierre series of northern Montana. Since the Pierre shales are noted for their selenium content large areas of Alberta are dangerous for grazing of stock when a large part of the diet is on the seleniferous plants for a long period of time. Byers considers that any soil with 0.4 to 0.5 PPM and any plant with 5.0 PPM as dangerous. The soils and plants of Alberta that were analyzed will therefore fall in this range.

The species A. bisulcatus and A. pectinatus serve as excellent "indicators" of seleniferous areas.

The analytical data show no quantitative relationship between the quantity of selenium in the soil and that absorbed by individual members of the same plant species, neither in the surface soils and the soil profile.

Different portions of the plant have different concentrations of selenium, the greatest amount being in the leaves and flowers.

References

1. Byers, H.G., and Lakin, H.W., Canadian Journal of Research, 17, 364 (1939).

2. Byers, H.G., U.S. Dept. Agric. Tech. Bull., No. 482, 530 (1935).

3. Wilcox, E.V., "Country Gentleman," Nov. 1935.

4. Williams, K.T., and Byers, H.G., Ind. Eng. Chem., 28, 912 (1936).

5. Williams, K.T., and Byers, H.G., Ind. Eng. Chem. Anal. Ed., 6, 296 (1934).

6. Hurd-Karrer, A.M., Jour. Agr., Research, 50, 413 (1935)

7. Alkali Disease or Selenium Poisoning, Bull. 311 (1937)

8. Harris, W.E., "The Distribution of Selenium in Alberta, Master's Thesis (1939).

9. Robinson, Dudley, Williams, and Byers, Ind. Eng. Chem. Anal. Ed., 6, 274 (1934).

10. Curl and Osborn, J. Assoc. Off. Agric. Chem., 21, 228 (1938).

11. The American Association of Petroleum Geologists, Stratigraphy of Plains of Southern Alberta, 1 - 12 (1931).

12. Noyes and Bray, Qualitative Analysis for the Rare Elements.

SECTION II

Further Study on Occurrence of Fluorides in Alberta Waters

Introduction

The survey on occurrence of fluorides in Alberta water supply was started by O.J. Walker and E.Y. Spencer in 1935 (1). This work was continued by G.R. Finlay in 1938 (2).

The object of the survey is to map out the endemic areas in Alberta of dental fluorosis. "Dental fluorosis" or "mottled enamel" is associated with the fluorine content of water. This fact was established in 1931 by Smith and her co-workers (3,4) and Churchill (5).

The effect of fluorine sets in during the period when teeth are calcifying within the gums (6) which takes place between the ages of six months and twelve years. It has been found (7) that the teeth become mottled when the fluorine content of water exceeds 1 p.p.m Once the teeth have been attacked the mottling cannot be removed by any method which is now available and it is therefore necessary to supply children with water which contains less than 1 p.p.m. of fluorine. This may be done by switching over from a water high in fluorine to a water low in fluorine, or by using a defluorite system which lowers the fluorine content to less than 1 p.p.m. (8).

Experimental Method

The fluorine content of waters is determined according to the methods adopted by the previous workers (1,2,8) in this laboratory.

Two methods are available, the modified Sanchis method, and the modified Armstrong method. The former method is used on all water samples and the latter only on waters containing over 1 p.p.m. of fluorine.

Sanchis (9) developed a method suitable for the determination of the fluoride content of waters. This colorimetric method depends upon the fading of the zirconium lake of the dye, sodium alizarin sulfonate, in acid solution, by the formation of the complexes $Zr\ F_5^{-}$, $Zr\ F_6^{=}$, $Zr\ F_7^{\equiv}$ etc. The distillation method adopted by Armstrong (10) and by Walker and Spencer (1) consists of distillation in the presence of silica to separate interfering elements, fluorine distilling over from an acid solution as hydrofluosilicic acid.

$$3\ H_2SO_4 + SiO_2 + 3\ CaF_2 \rightarrow H_2SiF_6 \uparrow + 3\ CaSO_4 + 2\ H_2O$$

The distillate, after concentration, is titrated with thorium nitrate using a solution of sodium alizarin-sulphonate as indicator. The end point is indicated by the appearance of the red color of the ~~zirconium~~ thorium lake.

At present the modified Sanchis method is used as follows: To a 100 c.c. sample of water are added 2.0 c.c. of 3.0N hydrochloric acid, 2.0 c.c. of 3N sulfuric acid, and 1.80 c.c. of indicator solution (made up to contain 0.17 mg. of sodium alizarin sulfonate and 0.87 mg. of C.P. zirconium oxy-nitrate, $ZrO(NO_3)_2.2H_2O$ per c.c.) The solution is heated just to boiling, allowed to stand for four hours or over night and compared with standards containing 0.0, 0.25, 0.45, 0.65, 0.85, 1.00, 1.25 and 1.5 p.p.m. fluorides which are treated in the same manner. The range may be extended by taking an aliquot of the original sample, usually 50 c.c., diluting to 100 c.c. and multiplying by the factor required. As sulfates affect the color of the lake, care must be taken in measuring the sulfuric acid, and the amount of indicator is also important. Where the fluoride content exceeds 1 p.p.m. a sulfate correction is applied.

For the modified Armstrong method the amount of water used is such that approximately 0.2 mg. of fluorine is present. After this is made alkaline to phenolphthalein with 0.2N sodium hydroxide it is concentrated to 50 c.c. placed in 250 c.c. distilling flask along with 20 c.c. of concentrated sulfuric acid and some glass beads. The flask is fitted with a thermometer extending into the

liquid and a dropping funnel is connected to a capillary tube also extending into the liquid so that water may be added from time to time. Water is added so that distillation commences at 110°C. and the distillation is continued until 75 - 100 c.c. of distillate is collected. Water is added through the funnel so that the temperature remains below 135°C. The distillate is made alkaline to phenolphthalein, and concentrated to 20 c.c. To this is added 20 c.c. of 95% ethyl alcohol, three drops of indicator which is a 0.5% aqueous solution of sodium alizarin sulfonate and then titrate with 0.2 N hydrochloric acid from red to yellow. Add 2 c.c. of buffer to maintain a constant pH during the titration with thorium nitrate. The buffer contains 0.4 moles of monochloroacetic acid and 0.4 moles of sodium chloroacetate in one litre. The solution is now transferred to a Nessler tube and titrated to a faint permanent pink with standard thorium nitrate solution from a 10 c.c. microburette. After subtracting the blank required for the formation of the thorium lake, which amounts to 0.05 c.c., the parts per million of fluorine in water is calculated. The thorium nitrate solution which is between 0.01 N and 0.02 N is standardized against a 0.02 N solution of sodium fluoride.

If the phosphate concentration in the water is suspected to be high it is necessary to carry out the dis-

tillation in the presence of 25 c.c. of 60% perchloric acid in place of the sulfuric acid or a double distillation with the sulfuric acid.

F^- in P.P.M.

Lab.No.	Place	Depth	Sanchis	Armstrong
783	Beaverlodge	250'	1.8	0.4
791	Halcourt	180'	4.2	1.7
793	Nobleford	150'	2.7	0.2
808	Raven	140'	3.0	0.6
811	Etzikom	715'	2.3	2.6
824	Carmangay	58'		0.1
832	Lethbridge	247'	2.7	1.3
837	Nobleford	90'	2.8	0.02
839	Lethbridge	310'	1.5	
850	Edmonton	360'	1.5	
865	Ponoka	37'	3.0	1.4
866	Ensign	240'	3.6	0.7
867	Penhold	195'	2.0	0.5
878	Daysland	80'	0.9	
879	Millet	67'	1.3	0.1
880	Gleicken		0.0	
881	Raymond		0.0	
883	Barons	96'	1.0	
884	Milk River		1.5	0.1
887	High River	96'	3.0	0.7
888	McLaughlin	30'	0.3	
889	Lacombe	92'	0.0	
890	Carbon	70'	0.5	
891	Olds	283'	1.3	0.5
896	Beiseker	110'	1.3	
898	S. Edmonton	130'	2.9	
904	Calgary			0.3
913	Lethbridge	206'	2.0	
915	Namaka	89'	1.5	
918	Pine Lake	130'	3.5	
919	Strathmore	180'	0.4	
920	Beiseker	123'	>3.0	1.6
921	Magnolia	10'	0.2	
922	Fairy Dell	317'	0.0	
923	Milk River		1.7	0.1
924	Cessford	32'	0.2	
925	Delia	35'	0.0	
926	Nanton	65'	1.3	0.1
927	Strathmore	22'	0.0	
928	Athabasca	60'	0.0	
929	Sedalia	12'	0.0	
930	Grimshaw	264'	0.5	
931	Claresholm	6'	0.0	
932	Wainwright	30'	0.0	
933	Delia	77'	0.1	
934	Elnora	140'	0.5	
935	Carbondale		1.10	0.1

F^- in P.P.M.

Lab.No.	Place	Depth	Sanchis	Armstrong
936	Streamstown	100'	0.5	
937	Cowley	400	3.0	2.1
938	Beaverlodge	8	0.5	
939	Beaver Crossing	30	0.5	
940	Rosyth		0.5	
941	Milk River		0.4	
942	Drumheller	City Water tap	0.1	
943	Lloydminster	12	2.7	0.3
944	Botha	40	0.3	
945	Mayerthorpe		0.3	
946	Trochu	110	0.7	
947	MacLeod	18	0.2	
948	Coleridge	21	0.6	
949	Hanna	100-108	0.0	
950	Chauvin	282	0.0	
951	Standard	80	0.9	0.8
952	Clandonald	76	0.5	
953	Tofield	35	0.5	
954	New Norway	60	0.3	
955	Youngstown	10	0.7	
956	Hanna	112-128	0.0	
957	Westerose	68	0.5	
958	Winfield-	4	0.5	
959	Westerose	18	0.0	
960	Mossleigh	198	0.0	
961	Heart Valley	21	0.5	
962	Ponoka	24	0.5	
963	Drumheller	170	0.3	
964	Westerose	61	0.0	
965	Bon Accord	35	1.0	0.1
966	Monarch	18	0.0	
967	Ponoka	Spring	0.7	
968	Bruderheim	16	0.0	
969	Bruderheim	30	0.0	
970	Bruderheim	24	0.0	
972	Coronation	38½	1.3	0.03
974	Del Bonita	293	1.1	0.2
975	Delburne	100	0.3	
976	Onoway		0.5	
977	Mundare	30	1.7	0.1
978	Sangudo	180	0.7	
979	Red Deer	90	2.0	0.5
980	Red Deer	80	1.7	0.8
981	Hanna	100	0.0	
982	Blackie	140	1.1	0.1
983	Strathmore	200	3.0	1.1
984	Strathmore	13	3.0	0.9

F^- in P.P.M.

Lab.No.	Place	Depth	Sanchis	Armstrong
985	Vulcan	105'	0.3	
986	Picture Butte	12	2.0	0.2
987	Grimshaw	26	0.7	
988	Chinook	70	0.5	
989	Nisbet		0.0	
990	Grimshaw	53	0.4	
991	Gainford	12	0.0	
992	Gainford	20	0.0	
993	Calgary	40	0.2	
994	Andrew		0.4	
995	Westlock	25	0.0	
996	Kingman		0.4	
997	Westlock	265	1.9	0.8
998	Andrew		0.5	
999	Fabyan	190	0.0	
1000	Edmonton		0.9	0.01
1001	Busby	40	0.5	
1002	Alcamdale	56	0.3	
1003	Castor	40	0.9	0.01
1004	Wakstao	24	0.1	
1005	Morinville	50	0.5	
1006	Grande Prairie		0.3	
1007	Claresholm	95	0.5	
1008	Huxley	90	0.1	
1009	Busby	60	1.1	0.4
1010	Wakstao	13	0.0	
1011	Cassils		2.5	1.6
1012	Burdette		0.3	
1013	Bowden	45	0.1	
1014	Bowden	26	0.3	
1015	Stavely	125	3.0+	1.1
1016	Stavely	135	2.8	2.5
1017	Stavely	135	3.0+	2.4

Summary

Both the colormetric and the titration methods for the determination of fluorides have been discussed in full. The colormetric method has been used for all of the water samples and the titration method for those which were found to contain 1.0 or more p.p.m. of fluorine by the colormetric method.

The results have been tabulated, showing the source of the water and the depth of well from which it was obtained.

The sulfate corrections on the Sanchis method are shown in the following section which deals with sulfates in water.

References

1. Walker, O.J., and Spencer, E.Y., Can. Jour. Research, B 15, 305 (1937).

2. Finlay, G.R., "The Occurrence of Fluorides in Alberta Waters." Master's Thesis (1939).

3. Smith, M.C., Lantz, E.M., and Smith, H.V., Science, 74, 244 (1931).

4. Smith, M.C., Lantz, E.M., and Smith, H.V., Arizona Agr. Exptl. Sta. Tech. Bull., 32, 254 (1931).

5. Churchill, H.V., Ind. Eng. Chem., 23, 996 (1931).

6. Dean, H.T., McKay, F.S., and Elvove, E., Public Health Rep., 53, 1736 (1938).

7. Smith, H.V., Ind. Eng. Chem. Anal. Ed., 6, 134 (1934).

8. Walker, O.J., Finlay, G.R., and Harris, W.E., Can. Jour. Research, B 17, 308 (1939).

9. Sanchis, J.M., I.E.C. Anal. Ed., 6, 134 (1934).

10. Armstrong, W.D., I.E.C. Anal. Ed., 8, 384 (1936).

SECTION III

Determination of Sulfates in Alberta Waters

Introduction

Sulfates are undesirable in waters for both domestic and industrial purposes when present in large concentrations.

Authoritative opinions appear to be at variance ~~diversified~~ regarding the purgative or cathartic effects of sulfates. Sulfates are present in blood and urine. The normal human blood serum contains over 0.02% of sulfate ions (2,3,14) and the average concentration in the blood plasma is 6.2 mg. of sulfur per 100 c.c. (4). The concentration in the urine and the kidneys is generally lower than in the blood. A healthy person secretes, daily, 18 g. of ethereal sulfuric acid (1). Russo (8) states that sulfate ions, when taken into the body, have a depressor action on the tone and in part on the automatic movements of the organs. According to Zörkendörfer (5) sulfites and sulfides are formed from sulfates in the intestine. Sulfates are in part reduced to hydrogen sulfide. The purgative action of the salt is independent of the amount of hydrogen sulfide formed, but is proportional to the amount of sulfate present. Iron salts which remove hydrogen sulfide to a large extent does not affect the purgative action. The latter is

considered due chiefly to osmotic action coupled with the removal of calcium ions. The flow of water from the tissues into the intestinal tract by the process of osmosis increases the volume of water sufficiently to produce a profuse discharge from the bowels. Nakashima (13) found that sulfates are only difficultly absorbed from the small intestine even when present in large concentrations.

Hypotonic mineral waters containing sulfates cause protracted diuresis (6) which appears to be due to a special action of the sulfates. According to Möller (9) the diuretic effect of combination of sulfate and theophylline is far greater than that which takes place with either alone. Solutions of sodium sulfate which are approximately isotonic increase the excretion of chlorides but slightly, but is markedly increased by the simultaneous action of sulfate and theophylline. Sulfates are rapidly eliminated with alkaline urine (7) but slowly with acid urine. They are excreted with an increased water elimination. After the sulfate administration the chloride excretion is increased only on an acid diet.

Möller (9) also states that sulfate infusions reduce the chloride concentration of the blood, while Stransky (10) claims that it is without influence of

the chloride exchange of the organisms. He studied the anion balance of Cl^-, $SO_4^=$, and $H_4(PO_4)^{-5}$ radicals when distilled water and Carlsbad water were ingested by rabbits. The sulfate ion is completely absorbed and it is only partly retained during the course of administration. The main effect observed was the retention of phosphates by the animals when they were given the mineral water. Since the same effect was obtained when sulfate solutions were given, the phenomenon is attributed not only upon the specific cation mixture of the mineral water but as a predominant action of the sulfate ion therein contained. Denis (11) studied the selective action of the kidney in regard to the excretion of inorganic salts. Experiments made on dogs and on rabbits in which $MgSO_4$, Na_2SO_4, $MgCl_2$, $NaCl$, Na_2HPO_4 were administered by the intestine and by intravenous injection, and the subsequent excretion of these salts followed by means of blood analysis, indicate a selective retention on the part of the kidney for the sulfate ions, which in one case were found to accumulate in the serum to a value of 3200% of its initial concentration. Hayman and Johnston (12) found that inorganic sulfates are less concentrated by the human kidney than creatinine or urea, perhaps because of reabsorption through the tubules. After intravenous injection of

sulfates, its concentration ratio approaches that of creatinine. Sulfate (4) passes freely in and out of the kidney in relation to the concentration of the sulfate in the surrounding sulfate - Locke fluid. Equilibrium is reached in fifteen minutes.

Daniels and Rich (14) carried out a number of experiments which were designed to determine whether the animal organism is able to synthesize the indispensable sulfur-containing amino acid, cystine, from inorganic sulfates. Inorganic sulfates added to a diet supplying an adequate amount of cystine-containing protein have no apparent important nutritive function. If the diet is deficient in cystine, the addition of inorganic sulfates does not produce normal growth, the rats being unable to utilize the sulfates in the production of cystine.

An interesting discovery was made by Högbom (15) on the geological and biological effects of sulfate bearing solutions on humus waters. After a dry spell lake levels sank very low. The exposed post-glacial soil was rich in sulfides which were oxidized to efflorescent sulfates. When the lakes rose, the sulfates were dissolved in the water and caused the precipitation of the humus compounds which they contained, thus affecting the fish and plants.

In industry it is important to have a water supply which is low in sulfates if possible. The presence of calcium and sulfate produce a hard adherent calcium sulfate scale (16, 18). Conditioning of boiler waters so that evaporation will not result in a deposition of a scale depends upon the sulfate concentration and boiler pressure (16). By maintaining sufficient carbonate or phosphate concentration at any given boiler pressure such that solid calcium carbonate or calcium phosphate is the stable solid phase rather than solid calcium sulfate, all hardness will be precipitated as carbonates or phosphates and no hard scale will be formed. According to Hamer (17) the carbonate-sulfate ratio is affected by the presence of sodium salt and changes in boiler pressure. If no sulfate scale is being formed, all the sulfate remains in solution and the ratio (sulfate in blowdown)/(sulfate in feed) is equal to the chloride ratio. If the sulfate is less than the chloride ratio then sulfate scale is being deposited, and conversely if greater, sulfate is going into solution. From these two ratios the amount of sodium carbonate to be added can be determined.

Sulfates in water present a problem also in the sugar industry (18). It interferes with the crystallization in sugar-making by increasing the amount of sugar

retained in the mother liquor. In cement making sulfates delay the setting and hardening process (19), and undoubtedly contribute to the destructive action on cement (20,21).

Sulfates in water have a few beneficial advantages in industry. For instance, beer of excellent flavor and stability is prepared from water high in sulfates (22). This beer is much lighter in color than that prepared from water low in sulfates. Waters of high sulfate content are also suitable for tanning heavy hides as they swell the skins exposing more surface for the action of the tanning liquors.

On the whole, it may be stated that waters containing a high concentration of sulfates are undesirable for domestic purposes and present a trying problem in the industries. According to the United States Public Health Service, drinking water should not contain more than 250 p.p.m. of sulfate.

Purpose of this Investigation

The purpose of this investigation was to find a rapid and reasonably accurate method to determine the sulfate content of Alberta waters in conjunction with the survey which has been and is being carried out on the fluoride content of Alberta waters.

Finlay (23) (the paper now in press) working in this laboratory found that sulfates caused serious errors in the determination of fluorine by the colorimetric method. The effect of sulfates is additive, so that a correction may be applied if the amount of sulfates present is known. In general, 300 p.p.m. $SO_4^=$ is equivalent to 0.1 p.p.m.F^-, although for very large amounts of sulfates the effect is not so great proportionately.

Discussion of Methods of Analysis

An extensive review of the literature has been made with the view to determine which method would be most satisfactory for the analysis of sulfates in Alberta waters. The factors, time and accurracy, were borne in mind. The possible methods for sulfate determination shall be discussed, omitting as much precise detail as possible.

The gravimetric method has been for a great number of years and is still employed for sulfate determinations.

This involves a series of weighings, precipitation, digestion, filtration, washing, drying, and final weighings. The method is time-consuming, the minimum length of time, for one determination, being six hours. It is very accurate and, except where occlusion and adsorption errors are high (25-29), is free from serious interference (24).

Several methods which might be classified as colorimetric have been suggested for the determination of sulfate (30-35). One method involves the precipitation of the sulfate as benzidine sulfate, the precipitate is diazotized and coupled with phenol (30) or with thymol (31 The intensity of the color is proportional to the amount of benzidine. In other methods the sulfate is precipitated as lead sulfate (32,36), benzidine sulfate (33,34), as barium lead sulfate with barium chromate (35), and the resultant precipitates are compared colorimetrically with their respective standards. Schroeder (24) considers colorimetric methods too complicated for routine analysis, even though they may be satisfactory for a limited number of determinations.

Since these two methods are time-consuming, they are considered unsatisfactory where time as well as accuracy are the important factors. The methods suggested in the literature as suitable for the rapid determin-

ation of sulfate may be roughly divided into three classes: (a) filtration methods; (b) those determinations in which a titration method is used, with internal or external indicators; (c) and turbidimetric methods.

(a) Filtration Methods

The benzidine method is probably the best known example of a filtration method (24). It has been the subject of extensive investigations in which the concentration of impurities, concentrations of reagents, temperature and method of titration, and the method of filtration and washing have all been carefully studied.

Raschig (37) first used benzidine hydrochloride to determine sulfates in coal analysis. Jacobson (38) first used the method to determine sulfates in water. The method (39-44, 51) consists in precipitating the sulfate by means of benzidine hydrochloride, as benzidine sulfate. The precipitate after filtration is suspended in water, and titrated in the hot with sodium hydroxide using phenolphthalein, or bromothymol blue as indicator (50). Other workers (46-49) titrated the precipitate with potassium permanganate.

A number of other methods require filtration and the filtrate or the precipitate is titrated using an external or internal indicator.

Such a method is that of Roemer (52) which is a

modification of Holliger's method (53). Sulfate is precipitated with standard barium chloride, the excess barium is precipitated as barium chromate with a standard chromate solution. The precipitates of barium sulfate and barium chromate are filtered off. The excess standard chromate, in the filtrate is titrated with standard ferrous ammonium sulfate using potassium ferrocyanide as indicator. Others add potassium iodide to the filtrate and titrate the iodine freed with sodium thiosulfate using starch indicator (29,53,54-60,62.)

The sulfate has also been precipitated with excess barium chromate (64,66-70.) The filtrate is titrated with excess standard ferrous ammonium sulfate and then back titrated with standard permanganate. Josephson (66) modified Andrew's method (64) by determining the excess chromate by iodometric titration. In other cases the various precipitating agents used are barium hydroxide (63), lead nitrate (65), barium phosphate (71) and the excess precipitating agents are titrated in the filtrate with various standard solutions.

In another method, which does not involve a filtration but which depends on a partial separation of the solution and solid, the solution is centrifuged and the volume of the barium or lead sulfate precipitate measured in a narrow graduated tube. The weight of the precipitate is determined from the volume (72-76). Klinke (77),

after precipitating with potassium chromate and barium chloride, titrates the centrifuged solution iodometrically. Another method is to centrifuge the solution after adding barium chloride (78), and to the filtrate is added excess sodium carbonate, then centrifuged, and the barium carbonate precipitate titrated with standard acid. A somewhat different method (36) is to dissolve the centrifuged precipitate of lead sulfate in sodium hydroxide and the color produced upon adding alkaline sulfide, compared with standards. Where a centrifuge is available this method is sometimes satisfactory for the routine determination of sulfate.

(b) Titration Methods

The above procedures require a filtration, which necessarily makes the methods rather long. Direct titration methods would have considerable advantage in regard to the speed with which a determination could be made.

Several methods which have been worked out for the titration of sulfate depend on the use of lead salts (79,80) with a few drops of potassium iodide as indicator. The end point is given by a permanent yellow color. According to a number of workers (81) this method is impractical and can be used in cases when time is more important than accuracy. In general, the lead sulfate which is precipitated is too soluble to make these methods

readily applicable to dilute solutions (24).

A number of methods are available for the determination of sulfate in which outside indicators are used to determine the end point. One of these consists of making yellow stains on white filter paper by adding a few drops of a solution containing the sodium salt of rhodizonic acid (82,91,96). The sulfate solution, in the presence of an acid, is titrated with a solution of barium chloride until a drop of the solution gives a red color to the test paper, In numerous methods, excess barium chloride is added and the excess determined by back titration employing various solutions and external indicators which are enumerated for brevity: 1. standard ammonium potassium chromate and "benzidine" paper (83); 2. standard sodium sulfate and congo red and ammonium dichromate (84); 3. standard chromate solutions and p.p'. diaminodiphenylamine paper (85), solution of lead salt (88), and ferrous thiocyanate (90) as external indicators; 4. excess standard dichromate titrated with standard ferrous ammonium sulfate using potassium ferrocyanide (86,87) or lead nitrate (88), as external indicators.

For routine analysis the use of outside indicators is too slow and subjects the method to inaccuracies.

In several titration methods internal indicators are used. In the method of Jellinik (95), the sulfate is precipitated with excess barium nitrate, the excess

is titrated with excess potassium chromate. The titration is finished with standard barium nitrate until a colorless supernatant solution is obtained. Another method depends on the hydrolysis of a salt of a strong base and a weak acid to give a basic reaction to the indicator - for example, to the sulfate solution, excess barium chloride is added and is titrated with potassium chromate in the presence of methyl red (97-99), phenolphthalein, bromothymol blue, phenol red, or cresol red (105). The excess barium chloride can be titrated with standard sodium carbonate to a faint pink end point of phenolphthalein (93), or the blue of thymolphthalein (94). Potassium stearate with bromothymol blue indicator has also been used (96). Another is the method proposed by Bahrdt (100-103,107). The excess barium is precipitated as barium palmitate, an excess of standard potassium palmitate is alkaline to phenolphthalein. Northall - Laurie (104) used barium carbonate suspension. A pink color develops due to the formation of barium sulfate and soluble alkali carbonate. The solution is titrated slowly with dilute acid until carbonates are changed to bicarbonates when phenolphthalein colors the solution again.

In a method which differs from the others, the excess barium chloride and potassium chromate is titra-

ted with rosolic acid, as internal indicator (108,109). In another method the excess barium is precipitated with ammonium dichromate, and the excess dichromate is titrated with sodium thiosulfate (106).

In many cases titration methods which depend on hydrolysis reactions are satisfactory. They are, however, subject to interference from the presence of phosphate and carbonate, and to some extent from other buffer salts, such as silicates and aluminates (24).

A method has been evolved which depends on the use of methyl red as an adsorption indicator (110). The method did not prove satisfactory for quantitative determination of sulfate.

An internal indicator method which seems to be convenient and rapid has been worked out recently in Germany by Strebinger and Zombory (111,112,115,117), and later adopted by others (113,114,116). In this excess standard barium chloride is added and is titrated back with standard sodium sulfate in the presence of the sodium salt of rhodizonic acid. The end point is denoted by the disappearance of the red barium salt of rhodizonic acid.

The number of methods by which the sulfate content of a solution, employing a direct titration in the presence of an internal indicator, can be determined, is

very limited. The method used in this laboratory, was that proposed by Schroeder (118) using a tetrahydroxyquinone indicator. This shall be discussed, later, in full. A method similar in principle to the Schroeder method was suggested by Ricci (119). The sulfate is titrated directly with standard lead nitrate solution with eosin as an internal indicator. The end point is indicated by the appearance of the red lead salt of eosin, $C_{20}H_6Br_4O_5Pb$. This method is not as effective as the Schroeder method for low concentrations of sulfate. Due to the relatively high solubility of lead sulfate and to the properties of both the eosin solution and the lead-eosin compound formed, the end point of such a titration will be markedly affected by changes in conditions, such as total volume, presence of foreign salts, etc. Erythosin has also been used as an internal indicator for the direct titration of sulfates with standard lead nitrate (120). The end point is denoted by a distinct blue color.

Other titration methods depend on conductivity measurements (121-135). This method has been studied with various precipitating agents (121,125 129,132,133), with various temperatures (121,128,130,133), affect of foreign substances (122,124,126,127,133), and the nature of the electrode and half cell (134). Conductivity methods have not been proved satisfactory for

routine analysis as special apparatus and titration curves are essential. Various other means of determining end points are by means of the refractometer and interferometer (136) and thermometric titrations (155,156).

(c) Turbidimetric Methods

Several different methods have been proposed as being applicable to the turbidimetric determination of sulfate. One method compares the turbidity, produced on the addition of barium chloride with those of standards (137,138,152-154). Another depends on nephelometric measurements in a colorimeter, of the barium sulfate precipitate (139,140,142,149,150). Photoelectric photometers have been employed to determine turbidity of the solutions (143-145,147,148,151). The Betz-Hellige method deals with the study of the Tyndall cone produced by colloidal barium sulfate (146). Others determine the depth of turbid liquid in a colorimeter (158,159). In a method which is much used at the present time, the depth of turbid liquid required to obscure a light filament is measured (29,157). A different method (160) is used to determine the end point by counting the time necessary to produce a yellow coloration of "turpeth" when a portion of titrated solution with barium chloride is added to a solution

of mercuric nitrate on a spot plate.

The turbidimetric method for the determination of sulfate has found wide application and in many instances is entirely satisfactory. Its chief disadvantages are: as ordinarily carried out the method requires the construction of a calibration curve; some special equipment aside from the regular analytical equipment is necessary; the range of concentrations over which the method may be used is quite short; the method is considerably influenced by other salts in the solution; and its accuracy in some instances is subject to considerable doubt.

Introduction to Analytical Determination of Sulfates

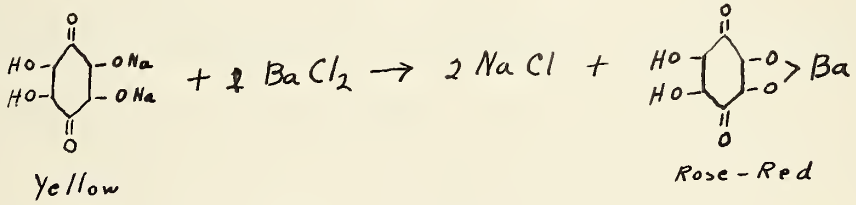
After a review of the literature, it was decided that the method proposed by Schroeder (24) with modifications (161,162) would prove the most satisfactory for the purposes of this laboratory. As it has already been stated, the number of methods which employ the direct titration of sulfate with an internal indicator is indeed limited. The two other methods (119,120), already discussed, have not proven entirely satisfactory because of the solubility of the lead salts employed in titrating the sulfate solution.

The indicator Schroeder used, was the disodium salt of tetrahydroxyquinone. It was made by treating glyoxal sodium bisulfite, prepared by treatment of acetaldehyde with nitric acid and sodium bisulfite, with a solution of sodium carbonate.

This salt is not stable in aqueous solution as the decomposition is quite marked even in as little a time as twelve hours. It is also inconvenient to make up fresh solutions of the indicator every time it is desired to be used. Schroeder found it very satisfactory to grind up a small amount of the indicator with a large amount of potassium chloride in a 1 to 400 ratio. The indicator used by Sheen, Kahler, and Betz (161), and that used in this laboratory (being the

same as the one used by Schroeder) was manufactured in the Betz laboratory. It is put on the market under the name of THQ and will be referred to as such hereafter. In this form the indicator is stable for a year or longer. In use, a few tenths of a gram of this indicator is added to the sample to be analyzed.

The indicator in solution is yellow, When the sulfate is precipitated as barium sulfate, by means of standard barium chloride in the presence of ethyl or denatured alcohol, excess barium chloride forms the rose-red barium salt of the indicator, which marks the end point as shown by the following equation.



A blank of 0.1 c.c. is subtracted from the total volume of standard barium chloride used in a titration. Schroeder found that if more than 0.6 mg. of phosphate is present, the blank should be increased to 0.6 c.c. The various other ions which may be tolerated without causing error are 7.5 mg. of carbonate, 5 mg. of aluminum, 25 mg. of silicate, and 15 or more milligrams of magnesium. Calcium has no effect as long as the addition of alcohol does not cause the precipitation of calcium sulfate. This precipitation must be pre-

vented. Hydroxides and chlorides are without effect. Iron above 0.1 mg. interferes and must be removed.

Skeen, Kahler, and Betz (161) extended Schroeder's maximum content of sulfate in a 25 c.c. sample, from 800 p.p.m. up to 30,000 p.p.m. or a 3 per cent solution of $SO_4^{=}$. They did this by using various standard barium chloride solutions, the concentrations varying from 1 c.c.= 1 mg. of $SO_4^{=}$ to 1 c.c.= 50 mg. of $SO_4^{=}$. They also used sodium chloride crystals to sharpen the end point and found that isopropyl alcohol could be used as a diluent instead of ethyl and denatured alcohols. Instead of applying a series of blanks as in Schroeder's method for phosphate, the concentration of which had to be known, they found that up to 60 p.p.m. the phosphate ion could be tolerated by decreasing the pH value of the sample before titration to approximately 4.0, with the aid of bromocresol green as indicator. With the exception of iron and aluminium, other ions normally present in boiler feed waters give no difficulty. Iron in both the ferrous and ferric state must be lower than 5 p.p.m. This is not a serious drawback to the method, as in boiler waters soluble iron will seldom be found to this extent with higher pH values, most iron being present in the insoluble form. Where iron is present in a sample in quantities above 5 p.p.m.

it should be removed prior to titration, as otherwise the THQ is colored green and destroyed. 6 p.p.m. of Al^{+++} cannot be tolerated. Here again, little difficulty is expected, as Al^{+++} is seldom found in appreciable concentrations in boiler waters. Below 100 p.p.m. the method is not as accurate as in higher concentrations. Their results checked with gravimetric determinations within an average of about 3 per cent.

Analytical Procedure

The procedure used in the determinations of sulfates in Alberta waters is similar to the method proposed by Schroeder (24) with the modifications of Sheen and Kahler (161) and further modifications given by W.H. and L.D. Betz (162).

Many samples of Alberta water contain iron and other suspended materials, and were therefore filtered discarding the first portion of the filtrate since part of the sulfate may be retained by the filter paper.

A 0.025N barium chloride solution was prepared and standardized gravimetrically; 1 c.c.= 1.2 mg. $SO_4^=$.

The procedure is as follows: Pipette a clear 25 c.c. sample into an Erlenmeyer flask of 250 c.c. capacity. Neutralize the acidity or alkalinity carefully to the acid side of phenolphthalein by 0.02N HCL or NaOH. The

temperature of the sample must be below 35°C. and preferably between 20° and 25°C. Add 25 c.c. of 95% ethyl alcohol. Introduce the THQ indicator by the standard dipper supplied which holds 0.2 mg. of indicator. Swirl the flask to dissolve the indicator. The solution is colored yellow. Titrate with the standard barium chloride solution from a 10 c.c. microburette until the yellow color changes to a rose-red color, swirling the flask continuously.

The sharpness of the endpoint is enhanced by the use of small amounts of silver nitrate resulting in the formation of the white silver chloride precipitate. When 4 c.c. of the barium chloride have been run in, add 1 c.c. of 0.1N $AgNO_3$. Silver nitrate is not added at the beginning of the titration, nor before 4 c.c. of barium chloride have been added because when silver nitrate is used in excess of the chloride concentration an intense cherry color will develop and the sample must be discarded. In solutions in which chlorides and bromides are present in high concentrations, use 1 c.c. of 0.2N$AgNO_3$.

The determination of the end point is aided by using a white background and a strong side illumination.

The most distinct endpoints are obtained when $BaCl_2$ is not used in excess of 10 c.c. If no endpoint is obtained by this volume, repeat with smaller volumes, 10,5, or 1 c.c., diluted to 25 c.c. with distilled water. By such means, up to 10,000 p.p.m. of sulfates can be determined. If the concentration is greater than this value, a more concentrated barium chloride solution may be used (1c.c. = 4 mg. $SO_4^=$). Endpoints are good with larger volumes of barium chloride but are not as intense in color as when the above volume restriction is observed.

If phosphates are known to be present, add 3 drops of 0.04% bromo cresol green indicator and neutralize, in the manner described, to the yellow range of this indicator. After neutralizing, proceed in the manner discussed. To increase the phosphate tolerance, use smaller volumes of sample and dilute to 25 c.c. Since it is important to keep the volume at a minimum, neutralize to the yellow range of bromo cresol green with 0.5NHCl, and use 1 c.c. of $0.2NAgNO_3$.

It is important that the solution is continually swirled throughout the whole titration. The standard barium chloride is introduced at a steady flowing rate until the end point is approached, then proceed by adding 2 or 3 drops at a time.

The end point of this titration is determined by the permanent change in color from yellow to rose-red and not by recognition of a certain depth of rose-red. Prior to the rose-red end point, the solution may acquire a light brown color, the color change from yellow to rose-red is not abrupt. For this reason an operator must run a sufficient number of tests to become acquainted with the color characteristics of the indicator.

In many samples of Alberta waters, the end point is reached before 4 c.c. of barium chloride have been added, and thus no silver nitrate is used. The end point, although being less sharp, can be determined after one becomes familar with this indicator.

Results

A number of synthetic waters were made up with known concentrations of sulfate, added as sodium sulfate. The effect of various ions at different concentrations, and pH's, were studied. The results obtained are tabulated. The tables are self-explanatory. Table I shows the results obtained for known concentrations of sulfate with the absence of all ions except those required in this titration method. A blank of 0.1 c.c. is subtracted from the volume of standard barium chloride used. The results throughout are expressed as p.p.m. i.e. parts of the ion considered per million parts of water.

Table II shows the effect of single ions.

Table III The addition of two or more ions.

Table IV Comparison of the results obtained by the titration method with the gravimetric method on samples of Alberta water.

Table V The results obtained on analysis of Alberta waters for sulfate. The tabulation shows the locality from which the sample was taken, the volume of sample used, and the volume of the standard barium chloride used in the titration. The results are expressed as parts of sulfate per million parts of water i.e. PPM.

Note: BCG = bromo cresol green. Wherever this indicator has been used in neutralizing the solution with hydrochloric acid it is shown by "BCG" All other solutions are neutralized with hydrochloric acid using phenolphthalein indicator.

Table VI shows the sulfate corrections from Fig. I applied to the fluoride content of waters by the colorimetric method.

Table I

Lab. No.	$SO_4^=$ Present PPM	$SO_4^=$ Found PPM	Difference %
44	49.2	49.5	+0.7
18	249	248	-0.4
19	249	248	-0.4
3	249	251	+0.5
82	973	935	-3.9
83	973	945	-2.8
84	1947	1952	+0.3
85	1947	1943	-0.2
102	10,000	10,144	+1.4
103	10,000	10,040	+0.4

Table II Effect of Single Ions

Lab. No.	$SO_4^=$ Present PPM	$SO_4^=$ Found PPM	Ca^{++} Present PPM	Difference %	
4	249	243	20	-2.7	
5	249	243	40	-2.7	
22	249	232	40	-6.8	
31	249	232	40	-6.8	
23	249	233	60	-6.4	
24	249	232	60	-6.8	
25	249	235	60	-5.8	
26	249	232	60	-6.8	
32	249	237	200	-5.0	
54	249	238	200	-4.7	
33	249	234	401	-6.2	
34	249	239	401	-4.2	
35	249	235	401	-5.8	
88	973	895	100	-8.	
89	973	1002	100	+3.	
87	973	906	200	-7.	
			Mg^{++}		
11	249	250	12	+0.1	
12	249	248	24	-0.4	
13	249	251	36	+0.5	
14	249	253	36	+1.5	
15	249	254	61	+1.5	
36	249	253	122	+1.5	
37	249	253	122	+1.5	
38	249	262	243	+5.0	
39	249	252	243	+1.1	
40	249	256	243	+2.6	
90	973	1011	122	+3.8	
91	973	1001	122	+2.8	
			Zn^{++}		
48	249	247	16	-1.0	
46	249	252	33	+1.0	
49	249	249	33	0.0	
47	249	213	65	Masked end point	
			$CO_3^=$		
62	249	248	36	-0.4	
63	249	252	72	+1.0	
77	249	247	72	-0.8	BCG
64	249	273	360	+9.5	
65	249	266	360	+6.6	

Lab. No.	$SO_4^{=}$ Present PPM	$SO_4^{=}$ Found PPM	$CO_3^{=}$ Present PPM	Difference %	
78	249	244	360	-2.2	BCG
66	249	274	720	+9.8	
95	973	1,084	360	+11.3	
96	973	957	360	-1.7	BCG
104	10,000	11,400	360	+14.0	
105	10,000	10,230	360	+2.3	BCG
			HCO_3^{-}		
68	249	270	37	+8.3	
76	249	244	37	-2.2	BCG
67	249	278	73	+11.5	
75	249	242	73	-3.2	BCG
97	973	1,227	366	+26.	
98	973	977	366	+0.4	BCG
107	10,000	12,220	366	+22.	
106	10,000	10,390	366	+3.9	BCG
			$PO_4^{\equiv}$		
72	249	254	32	+2.4	BCG
73	249	255	63	+2.4	BCG
74	249	261	95	+5.0	BCG
101	973	990	63	+1.7	BCG
100	973	1,114	158	+14.4	BCG
108	10,000	10,300	63	+3.0	BCG
			Fe^{+++}		
58	249	251	3.3	+0.8	
57	249	311	9.3	25.0	
56	249		19.0	No end point	
#109	973	1,000	187	+2.7	
#110	973	958	187	-1.6	
#113	973	985		+2.0	
			Fe^{++}		
61	249	256	6	+3.0	
60	249	269	14	+8.0	
59	249	273	28	+10.0	

Table III Effect of Two or More Ions

Lab. No.	$SO_4^{=}$ Present PPM	$SO_4^{=}$ Found PPM	Ca^{++} Present PPM	Mg^{++} Present PPM	Difference %		
16	249	243	100	61	-2.6		
41	249	243	200	122	-2.6		
42	249	236	200	122	-5.3		
43	249	237	200	122	-4.9		
81	249	239	200	122	-4.0		
45	249	237	200	122	-4.9		
92	973	971	200	122	-0.2		
93	973	1002	200	122	+2.9		
					Zn^{++}	Difference %	
55	249	254		122	33	+1.4	
53	249	243	200		33	-2.8	
50	249	248	200	122	33	-0.6	
51	249	249	200	122	33	0.0	
					$CO_3^{=}$	HCO_3^{-}	Difference %
70	249	255	100		36	37	+2.4
69	249	261	20		36	37	+4.6
79	249	247	100	61	180	366	-0.8 BCG
80	249	254	100	61	180	366	+1.9
99	973	1002			360	366	+2.9 BCG

Table IV Analysis of Alberta Waters Gravimetric Comparison

Lab. No.	$SO_4^{=}$ Titration PPM	$SO_4^{=}$ Gravimetric. PPM	Difference %	
824	3,338	3,490	-4.4	
837	241	214	12.0	
832	58	52	12.0	
883	4,455	4,458	-0.1	
930	990	887	12.	
935	397	345	15.	
943	10,070	10,722	-6.	
952	1,250	1,130	11.	
955	562	496	13.	
972	4,438	4,554	-2.5	
974	196	174	12.	
975	255	251	1.6	BCG
977	6,470	6,707	-3.4	
980	390	346	12.	
981	550	496	0.8	
983	241	220	9.5	
983	218	220	1.0	BCG
987	1,411	1,292	9.0	
987	1,262	1,292	-2.0	BCG
988	926	905	2.3	
990	1,081	966	12.0	
990	955	966	-1.0	BCG
993	1,046	931	12.0	
993	909	931	-2.2	BCG
999	389	310	25.	
999	299	310	-3.5	BCG
1000	2,921	2,726	7.0	
1000	2,681	2,726	-1.5	BCG

Table V Analysis of Sulfates in Alberta Waters

1 c.c. $BaCl_2$ = 1.185 mg. $SO_4^{=}$

Lab. No.	Location	Sample c.c.	$BaCl_2$ c.c.	$SO_4^{=}$ Titration PPM
824	Carmangay	2.0	5.635	3340
808	Raven	25.	0.03	1.0
837	Nobleford	25	5.075	240
866	Ensign	25	2.635	100
791	Halcourt	25	0.05	2.0
793	Nobleford	5.07	6.10	1430
823	Sedgewick	10.14	6.95	810
832	Lethbridge	25	1.225	60
783	Beaverlodge	25	4.80	230
839	Lethbridge	10.14	6.073	700
850	Edmonton	25	0.11	5
865	Ponoka	25	0.23	11
867	Penhold	25	0.705	30
904	Calgary	25	0.83	40
912	Didsbury	25	5.95	280
913	Lethbridge	10.14	1.125	130
878	Daysland	10.14	9.36	1090
879	Millet	25	3.02	140
880	Gleicken	25	0.075	4
881	Raymond	25	0.0	0
883	Barons	2.0	7.515	4460
887	High River	10.14	5.155	600
888	McLaughlin	10.14	6.005	700
889	Lacombe	25	2.90	140
890	Carbon	10.14	8.10	800
891	Olds	25	3.28	160
896	Beiseker	2.0	4.22	2500
811	Etizkom	25	0.15	7
919	Strathmore	25	2.745	130
920	Beiseker	25	3.38	180
921	Magnolia	25	0.375	20
922	Fairy Dell	25	0.425	20
923	Milk River	2.0	5.19	3080
924	Cessford	5.07	5.94	1390
925	Delia	5.07	4.295	1000
926	Nanton	5.07	4.075	950
927	Strathmore	25	3.69	180
928	Athabasca	25	0.685	30
929	Sedalia	25	2.57	130
930	Grimshaw	5.07	4.24	990
931	Claresholm	25	1.05	50
932	Wainwright	25	5.374	280

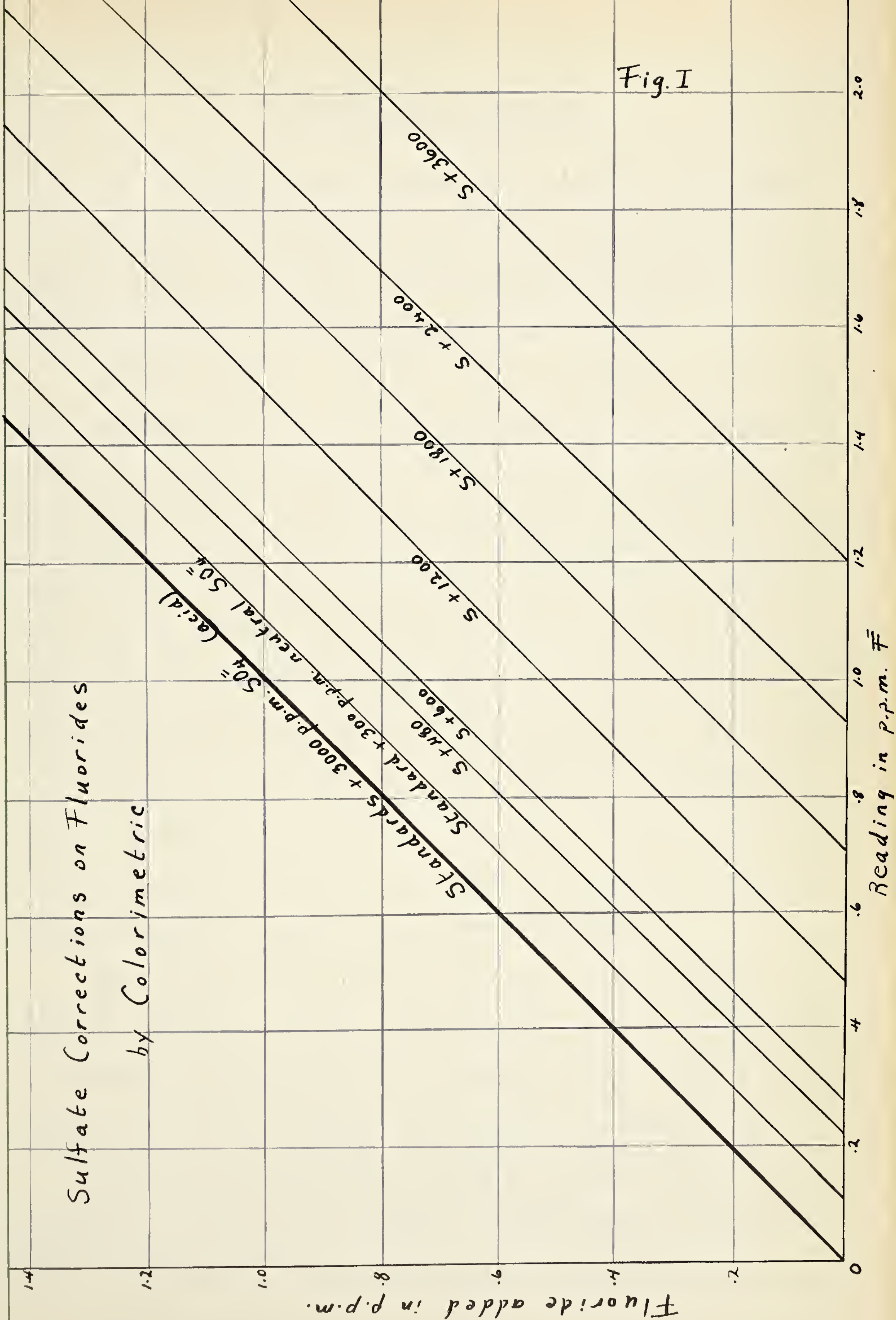
Lab. No.	Location	Sample c.c.	$BaCl_2$ c.c.	$SO_4^=$ Titration PPM
933	Delia	5.07	4.505	1050
934	Elnora	5.07	5.305	1240
935	Carbondale	25	8.385	400
936	Streamtown	25	5.0	240
937	Cowley	25	0.13	6
938	Beaverlodge	25	0.095	5
939	Beaver Crossing	25	1.77	8
940	Rosyth	25	7.30	350
941	Milk River	25	9.03	430
942	Drumheller	25	0.90	40
943	Lloydminster	1.0	8.5	10070
944	Botha	25	6.0	280
945	Mayerthorpe	25	1.60	8
946	Trochu	25	7.425	350
947	MacLeod	25	1.625	80
948	Coleridge	25	6.15	290
949	Hanna	10.14	5.07	1180
950	Chauvin	25	0.20	10
951	Standard	2.0	4.3	2550
952	Clandonald	5.07	5.35	1250
953	Tofield	5.07	3.66	860
954	New Norway	10.14	4.0	470
955	Youngstown	10.14	4.805	560
956	Hanna	10.14	5.20	610
957	Westerose	10.14	4.62	540
958	Winfield	25	0.125	6
959	Westerose	25	0.15	7
960	Mossleigh	15	5.9	470
961	Heart Valley	3.0	5.3	2290
962	Ponoka	25	3.9	190
963	Drumheller	5.07	5.65	1320
964	Westerose	25	0.365	2
965	Bon Accord	2.0	6.28	3720
966	Monarch	25	2.89	140
967	Ponoka	25	5.045	240
968	Bruderheim	25	0.3	15
969	Bruderheim	25	0.55	30
970	Bruderheim	25	2.0	95
971	Cold Lake	15	5.78	460
972	Coronation	2.0	7.49	4440
973	Cold Lake	25	7.26	340
974	Del Bonita	25	4.14	200
975	Delburne	25	5.38	255
976	Onaway	25	0.135	6
977	Mundare	1.0	5.46	6470
978	Sangudo	25	1.07	60
979	Red Deer	25	0.16	8

Lab. No.	Location	Sample c.c.	$BaCl_2$ c.c.	$SO_4^=$ Titration PPM
980	Red Deer	25	8.235	390
981	Hanna	5.07	2.439	550
982	Blackie	10.14	4.525	530
983	Strathmore	25	4.6	220
#984	Strathmore	25	7.10	340
985	Vulcan	25	1.545	70
986	Picture Butte	1.0	7.325	8680
987	Grimshaw	5.07	5.40	1260
988	Chinook	10.14	7.925	930
989	Nisbet	25	0.085	4
990	Grimshaw	10.14	8.17	960
991	Gainford	25	0.165	8
992	Gainford	25	0.25	12
993	Calgary	10.14	7.775	910
994	Andrew	25	1.20	60
995	Westlock	25	0.52	25
996	Kingman	25	0.125	6
997	Westlock	25	0.335	16
998	Andrew	25	0.425	20
999	Fabyan	25	6.3	300
1000	Edmonton	2.0	4.525	2680
1001	Busby	25	0.26	12
1002	Alcamdale	25	3.905	180
1003	Castor	25	6.22	300
1004	Wakstao	25	0.235	11
1005	Morinville	25	0.20	10
1006	Grande Prairie	25	0.66	30
1007	Claresholm	25	4.94	230
1008	Huxley	25	8.91	420
1009	Busby	25	0.145	7
1010	Wakstao	25	4.38	210
1011	Cassils	25	9.25	440
1012	Burdette	10.14	9.10	1060
1013	Bowden	25	0.25	12
1014	Bowden	25	0.149	7
1015	Stavely	25	1.30	50
1016	Stavely	25	2.05	100
1017	Stavely	25	1.10	50

Table VI Sulfate Correction applied to Fluoride

		F^- in PPM		
Lab. No.	$SO_4^=$ PPM	Colori-metric	Titra-tion	Colori-metric Corr.
783	230	1.8	0.4	1.8
791	2.0	4.2	1.7	4.2
793	1430	2.7	0.2	2.0
808	1.0	3.0	0.6	3.0
811	7	2.3	2.6	2.3
824	3340	2.4	0.1	1.2
832	60	2.7	1.3	2.7
837	240	2.8	0.02	2.8
865	11	3.0	1.4	3.0
866	100	3.6	0.7	3.6
867	30	2.0	0.5	2.0
879	140	1.3	0.1	1.3
887	600	3.0	0.7	2.8
891	160	1.3	0.5	1.3
839	700	1.5		1.3
850	5	1.5		1.5
878	1090	0.9		0.6
883	4460	1.0		0
896	2500	1.3		0.4
913	130	2.0		2.0
920	180	>3.0	1.6	3.0
923	3080	1.7	0.1	0.6
926	950	1.3	0.1	0.9
935	400	1.1	0.1	0.9
937	6	3.0	2.1	3.0
943	10070	2.7	0.3	0
951	2550	0.9	0.8	0
965	3720	1.0	0.1	0
972	4440	1.3	0.03	0
974	200	1.1	0.2	1.1
977	6470	1.7	0.1	0
979	8	2.0	0.5	2.0
980	390	1.7	0.8	1.6
982	530	1.1	0.1	0.9
983	220	3.0	1.1	2.9
984	340	3.0	0.9	3.0
986	8680	2.0	0.2	0
997	16	1.9	0.8	1.9
1000	2680	0.9	0.01	0
1003	300	0.9	0.01	0.9
1009	7	1.1	0.4	1.1
1011	440	2.5	1.6	2.4
1015	50	3.0+	1.1	3.0
1016	100	2.8	2.5	2.8
1017	50	3.0+	2.4	3.0

Fig. I


Sulfate Corrections on Fluorides by Colorimetric
S + 3600
S + 2400
S + 1800
S + 1200
S + 600
S + 480
Standard + 300 p.p.m. neutral $SO_4^=$
Standards + 3000 p.p.m. $SO_4^=$ (acid)
Reading in p.p.m. F
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
Fluoride added in p.p.m.
0
.2
.4
.6
.8
1.0
1.2
1.4

Discussion of Results

The average error from table I is ± 1.1%. These results are unimportant, outside of showing that the method can be applied to sulfate determination in waters, since no water can be obtained free of ions.

The presence of calcium ions, as shown in Table II tend to give increasingly lower results with increasing concentrations of calcium; the average lowering from 20 to 200 p.p.m. of Ca^{++} being approximately -6%. On the other hand, magnesium ions tend to give high results, the effect increasing with increasing concentration, the average error being +2% from 12 to 240 p.p.m. of Mg^{++}. The lowering of the sulfate values caused by the presence of calcium is decreased to about -3% when magnesium is also present as is shown in Table III. This knowledge is of some importance since magnesium and calcium are always present together in Alberta waters.

Zinc can be tolerated up to 30 p.p.m. with no serious effect. Above this concentration the end point is masked. Zinc is found, at the most, as traces in waters, so no difficulty would be encountered here.

Carbonates give high results, one was found to be +14% with 360 p.p.m. of $CO_3^{=}$ in 10,000 parts of sulfates. With increasing concentrations of carbonate, the values for sulfate were found to increase, on the average by

about +9%. On neutralizing the solution with acid using bromo cresol green (BCG) instead of phenolphthalein indicator, the errors due to carbonates were found to be only ±1.4%. In most cases, using this indicator, the concentration of sulfate tend to be slightly lower than the theoretical amount.

Bicarbonates affect the sulfate determination still more seriously. With as low as 37 p.p.m. of HCO_3^-, the error was +8.3% and with 366 p.p.m. the average error was +24%. Using bromo cresol green indicator this error was decreased to ±2.4%. Phosphates can be tolerated up to 60 p.p.m. if the solution is neutralized to the acid side of bromo cresol green with an error of +2.4%. The error increases up to 14% with 158 p.p.m. of $PO_4^{\equiv}$.

Iron in both the ferric and ferrous state must be maintained lower than approximately 5 p.p.m. This is no serious drawback since iron in Alberta waters do not exceed this value as is shown by the following section on the "Determination of Iron in Alberta Waters". Waters were made up with exceedingly high concentrations of iron to attempt to determine the sulfate content after its removal. This was done by adding excess standard barium chloride, making alkaline phenolphthalein with 10% potassium hydroxide, filtering, washing and diluting to

100 c.c. 25 c.c. of the filtrate is neutralized with acid, and 25 c.c. of ethyl alcohol, 1 c.c. of silver nitrate, a dipper of THQ are added and the resulting solution titrated with standard sodium sulfate until the red of the indicator is changed to yellow which marks the end point. From this the original sulfate content may be calculated. The method shows that the indicator THQ can be used reversibly to form again the sodium salt of the indicator.

Table III gives the results obtained when two or more different ions are present. It is interesting to note that the error caused by the presence of calcium, magnesium, carbonate, and bicarbonate, is relatively small in comparison to the error when any of these is present alone.

Table IV shows a comparison between the titration and gravimetric methods on a number of Alberta waters. The average difference of the thirteen waters mentioned in this table is ±2.4%. The average difference for seven other waters is approximately 12%. This cannot be taken as a conclusive result since the phosphate, carbonate, and bicarbonate correction was not applied to these particular samples. The table also shows a comparison of values obtained when a sample was neutralized in the presence of phenolphthalein and of bromo cresol green.

With the former indicator the results are usually considerably higher than the gravimetric values, while with the latter indicator the values are slightly lower. Although bromo cresol green indicator should be used in most samples of Alberta waters, it cannot be used in all waters because in the absence of carbonates, bicarbonates and phosphates, this indicator causes the results of the sulfate analysis to be very low, and especially when calcium and magnesium are present in high concentrations.

Table V gives the results obtained on the analysis of 127 samples of Alberta waters. The sulfate content was found to vary from 0.0 to 10,000 p.p.m. for different waters obtained from different localities in Alberta.

The sulfate correction is applied to the fluoride content of water and the results are shown in Table VI. A few of the results show some agreement between the titration method and the corrected colorimetric method. The majority of cases show a wide discrepancy which cannot be accounted for at the present.

Water sample 984 was strongly colored. A sample of 25 c.c. was decolorized, after making alkaline, with norite, filtered and carefully washed. An aliquot part of the filtrate was then titrated.

Summary

A method for the determination of sulfate in water has been described in full. The effect of different ions at various concentrations and means of lessening the error has been discussed. Ions which affect this method are iron, phosphates, carbonates and bicarbonates. Iron is not found in Alberta waters above the limits which can be tolerated. Phosphates can be tolerated up to 60 p.p.m. if the solution is neutralized in the presence of bromo cresol green indicator. With this same indicator, carbonates and bicarbonates can be present in large concentrations without materially affecting the results.

The rapid, direct titration of sulfates may be considered accurate to within ±3% with the gravimetric method. The method is time saving, one titration can be completed in less than fifteen minutes, where at least six hours are required for the gravimetric determination. The accuracy and rapidity of this method may be considered greater than other methods already described, and the range over which it can be used is also larger. Although in this laboratory the sulfate content has only been determined up to 10,000 p.p.m. it can be used for much larger concentrations by using a more concentrated standard barium chloride solution.

The values found for 127 waters varied from 0.0 to 10,000 p.p.m. of sulfate and the sulfate correction applied to the fluoride content of waters found by the colorimetric method.

References

1. Tollens, C., Z. physiol. chem., 67, 138 (1911)

2. Huebner, W., and Meyer-Bisch, R., Biochem. Z., 122, 120 (1921).

3. Loeb, R.F., and Benedict, E.M., J. Clin. Investigation, 4, 33 (1927).

4. Conway, E.J., and Kane, F., Biochem. J., 28, 1760 (1934).

5. Zörkendörfer, W., Arch. exptl. Path. Pharmakol., 161, 437 (1931).

6. Goldberger, J., Z. Urol 25, 512 (1931).

7. Moraczewski, W.V., and Sluvenski, R., Biochem. Z., 272, 268 (1934).

8. Russo, G., Boll. soc. ital. biol. sper. 4, 208 (1929).

9. Möller, K.O., Arch. exptl. Path. Pharmakol. 126, 159 (1927).

10. Stransky, E., Biochem. Z., 122, 1(1921).

11. Denis, W., J. Biol. Chem., 55, 171 (1923).

12. Hayman Jr., J.M., and Johnston, S.M., J. Clin. Investigation, 11, 607 (1932).

13. Nakashima, K., J. Biochem (Japan), 4, 277 (1924).

14. Denis, W., J. Biol. Chem., 49, 311 (1921).

15. Högbom, A.G., Bull. Geol. Inst. Univ. Upsala, 18, 239 (1922).

16. Hall, R.E., Fischer, C., and Smith, G.W., Iron and Steel Engr., 1, 312 (1924).

17. Hamer, P., Chem. Eng. Congr. World Power Conf., (1936) Advance proof No. L5, 24pp.

18. Peck, S.S., Intern. Sugar, J., 13, 357 (1911).

19. Grün, R., Zement 25, 1(1936).

20. Sartori, A., Chem. Ztg., 39, 957 (1915).

21. Scheelhase, Z. Ver. Deutsch. Arch u Ing. (16) 1913 through Mitt. zent. Ford. Deutsch. Port. Zement Ind., 2, 264.

22. Maurer, K., Z. ges. Brauw. 34, 589 (1912).

23. Findlay, G.R., Master's Thesis (1939).

24. Schroeder, W.C., Ind. Eng. Chem. Anal. Ed. 5, 403 (1933).

25. Allen, E.T., and Johnston, J., J. Am. Chem. Soc., 32, 588 (1910).

26. Hahn, F.L., and Keim, R., Z. anorg. allgem. Chem., 206, (1932).

27. Rudnev, N.A., Uchenuie Zapiski Kazan. Gosudarst. Univ. (Sci. Rept. State Univ. Kazan) 90, 1054 (1930).

28. Popoff, S., and Neuman, E.W., Ind. Eng. Chem. Anal. Ed., 2, 45 (1930).

29. McBride, R.S., and Weaver, E.R., J. Ind. Eng. Chem., 5, 469 (1913).

30. Kahn, B.S., and Leiboff, S.L., J. Biol. Chem., 80, 623 (1928).

31. Cuthbertson, D.P., and Tomprett, S.L., Biochem. J., 25, 1237 (1931).

32. Babkin, M.P., Lab. Prakt. (U.S.S.R.) 1939, No. 6, 19-21.

33. Yoshimatsu, S., Tohoku J. Exptl. Med. 7, 553 (1926).

34. Ibid, 119 (1926).

35. Lang, K., Biochem. Z., 213, 469 (1929).

36. Iokhel'son, D.B., Ukrain. Khem. Zhur., 9, Wiss. Teil 25 (1934).

37. Raschig, F., Z. angew. Chem. 16, 617,818 (1903).

38. Jacobson, Illinois Water Survey, Bull. 8, 112 (1911)

39. Bruckmiller, F.W., U. Ind. Eng. Chem. 7, 600 (1915)

40. Bruckmiller, F.W., Chemist. Analyst 11, 20 (1914).

41. " " " J. Ind. Eng. Chem. 7, 600 (1915).

42. Drummond, J.C., Biochem. J., 9, 492 (1915).

43. Rosenheim, O., and Drummond, J.C., Biochem. J. 8, 143 (1914).

44. Kuisel, H.F., Helv. Chim. Acta, 18, 332 (1935).

45. Lobstein, E, and Ancal, M., Ann. chim. anal, chim. appl. 15, 389 (1933).

46. Christie, A.W., and Martin, J.C., California Exp. Sta. Soil Science 4, 477 (1917).

47. Hibbard, P.L., Soil Sci., 8, 61 (1919).

48. Marsden, A.W., and Pollard, A.G., J. Soc. Chem. Ind., 56, 464 (1937).

49. Gollan, J., and Christen, C., Anales Asoc. quím. argentina, 24, 144 (1936).

50. Chatron, Bull. Soc. chim. biol., 3, 300; J.pharm. chim., 13, 244,321,425 (1931).

51. Synder, S., Chemist-Analyst, 20, No. 6,8 (1931).

52. Roemer, H., Z. anal. chem., 49, 490 (1910).

53. Holliger Z. and Chem, 49,84 (1910).

54. North, H., Am.J. Pharm. 86, 249 (1914).

55. Kuhlmann, J., and Grassfeld,J., Z. Nahr. Genussm. 43, 377 (1922).

56. Kolthoff, I.M., Rec. trav. chim., 40, 686 (1921).

57. Chabot, G., Bull. assoc. inst. sup. ferm. Gand, 26,; Ann. soc. brasseurs 34, 175 (1925).

58. Köszegi, D., Z. anal. Chem. 77, 203 (1929).

59. Schmidt, R., Z. anal. Chem., 82, 353 (1930).

60. Gusev, N., Hydrochem. Material (U.S.S.R.), 9, 3(in German 16) 1936.

61. Rivett, A.C.D., Chem. News, 118, 253 (1919).

62. Giral, J., Anales soc. espan. fis. quim., 20, 577 (1922).

63. Benesch E., Chem. Ztg., 47, 366 (1923).

64. Andrews. J.R., Ind. Eng. Chem. Anal. Ed., 3, 361 (1931).

65. Tananaev, N.A., J. Chem. Ind. (Moscow) 8, 939 (1931).

66. Josephson, B., Analyst 64, 181 (1939).

67. Skorecki, W., Arch. Chem. Farm. 3, 218 (in French 230) (1937).

68. Nachtigall, G., and Raeder, F., Arch. Hyg. 100, 31 (1928); U.S. Pub. Health Eng. Abstracts E-789a, 56.

69. Foster, M.D., Ind. Eng. Chem. Anal. Ed.,8, 195 (1936).

70. Rothenbach, E., and Antelmann, H., Wochschr. Brau., 48,457,467, (1931).

71. Macchia, O., Z'industria chemica, 4, 480 (1929).

72. Hamburger, H.J., Proc. Acad. Sci. Amsterdam, 19, 115 (1916).

73. Hamburger, H.J., Sitz. d. Koninklyke Akad. van Wetenschappen te Amsterdam Apr. 28, 1916; Biochem. Z., 77, 168 (1916).

74. Arrhenius, O., and Riehm, H., Medd. Vetenskapsakad. Nobelinst. 6, No. 4, 69 (1926).

75. Arrhenius, O., J. Am. Chem. Soc., 44, 132 (1922).

76. Tariverdyan, A.K.h., Higiena i Sanitariya 1938, No.2, 73; Khim. Referat. Zhur., 2, No. 1, 67 (1939).

77. Klinke, K., Biochem. Z., 154, 171 (1924).

78. Vanstienberghe and Bauzil. Ann. chim. anal., 23, 210 (1918).

79. Mindalev. Z., Moscow Tech. Hochsch. Z. anal. chem., 75, 392 (1928).

80. Grigor'ev, P., and Korol, S., J. Chem. Ind. (Moscow) 7, 1004 (1930).

81. Medinskiǐ, Kh. B.; Nikopol'skaya, V.L.; and Trusov, M.D.; Zavodskaya Lab. 3, 230 (1934).

82. Giblin, J.C., Analyst 58, 752 (1933).

83. Dominikiewicz, M., Bull. trav. dept. chim. inst. hyg. etat (Poland) 31, No. 1,3 (German 6); Przemysl Chem. 14, 241 (1930).

84. Vernazzo, E., Industria chemica 4, 988 (1929).

85. Roth, H., Z. angew. Chem., 39, 1599, 1601 (1926).

86. Mitchell, A.D., and Smith, C., Proc. Chem. Soc., 25, 291; J. Chem. Soc. 95, 2198 (1910).

87. Precht, Z. anal. Chem. 18, 521 (1879).

88. Germuth, F.G., J. Am. Water Works Assocn., 19, 607 (1928).

89. Wildenstein, Z. anal. chem, 1, 323 (1862).

90. Werthum, E.; J. Am. Chem. Soc., 52, 1075 (1930).

91. Muller, R., Vom. Wasser, 12, 290 (1937).

92. Seyb, E., Vom. Wasser, 12, 307 (1937).

93. Chalmers, A., and Rigby, G.W.; Ind. Eng. Chem. Anal. Ed. 4, 162 (1932).

94. Schoch, E.P.; J. Ind. Eng. Chem., 19, 112 (1927).

95. Jellinek, K., and Ens, H.; Z. anorg. allgem. Chem. 124, 185 (1922).

96. Atkinson, H., Analyst 50, 590 (1925;51,81,140, (1926)

97. Briwul, A.A., Z. anorg. allgem. Chem. 156, 210 (1926).

98. Hamus, M., Chimie et industrie Special No. 227 (1927)

99. Jellinek, K., and Czerwinski, J., Z. anorg. allgem. Chem. 130, 253 (1923)

100. Bahrdt, A., Z. anal. Chem., 70, 109 (1927)

101. Kehren, M., and Stommel, H., Chem. - Ztg., 46, 913, 934 (1927).

102. Bahrdt, A., Chem - Ztg. 52, 163 (1928).

103. Kehren, M., and Stommel, H., Chem - Ztg., 52 (1928).

104 Northall - Laurie, D., Analyst 56, 526 (1931).

105. Balaknovski, S., and Ginsburg, F., Z. anal. Chem., 86, 344 (1931).

106. Photiadis, Ph., Z. anal. Chem., 91, 173 (1932).

107. Hamer, P., J. Soc. Chem. Ind., 54, 250 (1935).

108. Nazarenko, V.A., Zwodskaya Lab. 4, 515 (1935).

109. Vinogradov, A.V., Ann. chim. anal. chim. appl., 17, 285 (1935).

110. Batchelder, G., and Meloche, V.W., J. Am. Chem. Soc., 54, 1319 (1932).

111. Strebinger, R., and Zombory, L.V., Z. anal. Chem., 79, 1 (1929).

112. Zombory, L.V., Z. anal. Chem., 110, 278 (1937).

113. Mutschin, A., and Pollak, R.; Z. anal. Chem. 106, 385 (1936).

114. Raeder, M.G. Kgl. Norske Videnskab. Selskab Forh., 5, No. 8, 32 (1933).

115. Zombory, L.V., Magyar Chem. Folyoirat, 189 (1935).

116. Abrahamczik, E., and Blumel, F., Mikrochim. Acta, 1, 354 (1937).

117. Strebinger, R.; Zombory, L.V., and Pollak, L., Z. anal. Chem., 105, 346 (1936).

118. Schroeder, W.C., Ind. Eng. Chem. Anal. Ed., 5, 403 (1933).

119. Ricci, J.E., Ind. Eng. Chem. Anal. Ed., 8, 130 (1936).

120. Burg, W.V., Ind. Eng. Chem. Anal. Ed., 11, 28 (1939)

121. Bruno, A., and D'Auzay, P.T., Compt. rend., 154, 984; Ann. fals., 5, 237 (1912).

122. Dutoit, P., and Duboux, M., Bull. soc. chim., 13, 1068 (1914).

123. Harned, H.S., J.A. Chem. Soc., 39, 252 (1917).

124. Kolthoff, J.M., Z. anal. Chem., 61, 433 (1922).

125. Muller, E., and Wertheim, R., Z. anorg. allgem. Chem., 133, 411 (1924).

126. Zanko, A.M.; Sci. Mag. Chem. Cath. Katerinoslav 79 (1926).

127. Fehn, H., Jander, G., and Pfundt, O., Z. angew. Chem., 42, 158 (1929).

128. Jander. G., Z. angew. Chem., 42, 1037 (1929).

129. Mukai, S., Bull. Coll. Kyushu Imp. Univ., 4, 17 (1929).

130. Jander, G., Pfundt, O., and Schorstein, H., Z. angew. Chem., 43, 507 (1930).

131. Kolthoff, I.M., and Kameda, T., Ind. Eng. Chem. Anal. Ed., 3, 129 (1931).

132. Atanasiu, I.A., Velculescu, A.I., Z. anal. Chem., 90, 337 (1932).

133. Pfundt, O., Angew. Chem., 46, 200 (1933).

134. Christensen, B.C., Wymore, H., and Cheldelin, V.H., Ind. Eng. Chem. Anal. Ed., 10, 413 (1938).

135. Vaĭnshteĭn, G.M., Zavodskaya Lab., 7, 778 (1938).

136. Bečka, J., Z. physiol. Chem., 121, 288 (1922).

137. Collins, W.D., and Foster, M.D., Ind. Eng. Chem., 15, 1078 (1923).

138. Hibbard, P.L., Ind. Eng. Chem., 16, 804 (1924).

139. Denis, W., and Reed, L., J. Biol. Chem., 71, 205 (1926).

140. Pieters, H.A.J., and Hovers, J., Chem. Weekblad, 29, 188 (1932).

141. Hofer, K., Wärme, 54, 803 (1931); Chem. Zentr., 1931, II, 3372.

142. Mohler, H., Z. anal. Chem., 92, 15 (1933).

143. Rumpf, P., Bull. soc. chim., 53, 84 (1933).

144. Urbach, C., Mikrochemie, 14, 321 (1934).

145. Andreev, N.N., and Andreev, E.V., J. Gen. Chem. (U.S.S.R.) 4, 594 (1934).

146. Sheen, R.T., Kahler, H.L., and Ross, E.M., Ind. Eng. Chem. Anal. Ed., 7, 262 (1935).

147. del Campo, A., Burriel, F., and Escolor, L.G., Bol. acad. cienc (Madrid) 2, No. 7, 10 (1936).

148. Pucherna, J., Listy Cukrovar, 54, 376 (1936).

149. Grant, J., Power and Works Engr., 32, 23 (1937).

150. Besombes and Buron, Ann. serv. tech. hyg. Paris, 18, 219 (1938).

151. Toepfer, E.W., and Boutwell, P.W., Ind. Eng. Chem. Anal. Ed., 2, 118 (1930).

152. Hinds, J. Am. Chem. Soc., 18, 661 (1896); 22, 269 (1900).

153. Jackson, Ibid, 23, 799 (1901).

154. Muer, Ind. Eng. Chem., 3, 553 (1911)

155. Dean, M.P., and Watts, O.C., J. Am. Chem. Soc., 46, 885 (1924).

156. Dutoit and Grobet, J. chim phys., 19, 324 (1922.

157. Hall, R.E., Otto, H.A., and Jackson, H.A., Ind. Eng. Chem., 17, 409 (1925).

158. Hibbard, P.L., Ind. Eng. Chem., 16, 304 (1924).

159. Campbell and Hurley, J. Am. Chem. Soc., 33, 1112 (1911).

160. Damerell, V.R., and Strater, H.H., Ind. Eng. Chem. Anal. Ed., 6 19 (1934).

161. Sheen, R.T., Kahler, H.L., Betz, W.H. and Betz, L.D., Ind. Eng. Chem. Anal. Ed. 8, 127 (1936).

162. Betz, W.H., and Betz, L.D., "Directions for the Determination of Sulfates by THQ," (1939).

SECTION IV

Determination of Iron in Alberta Waters.

Introduction

Iron is not presumed to affect the sanitary qualities of a water supply, although its presence above certain amounts may affect adversely the public acceptance of such waters for drinking purposes. Iron in natural waters and in those receiving industrial wastes may be in the ferric or ferrous condition, soluble, colloidal or insoluble. Ferric iron is rarely found in solution in appreciable quantities except in acid waters. Insoluble or colloidal iron is likely to be all ferric (1).

The purpose of this investigation was to compare the results obtained from two methods for determining iron in natural waters that had been submitted by the Committee on Chemical Water Standards to its members.

These methods were suggested by Delaporte of the Department of Health at Toronto, and McCrady of the Ministry of Health at Montreal, and are modifications of the thioglycollic acid procedure suggested by earlier workers. Historically, the principles involved in this method for the determination of iron was first put forth by Lyons (2). The method depends on the color produced by thioglycollic acid and iron in a solution which is made faintly alkaline. The color so produced

has long been known. Andreasch (3) described it in detail and Claesson (4) claimed that he was quite aware of the reaction. They believed that the color produced was due to the formation of the complex ferric thioglycollate, $Fe(SCH_2COONH_4)_3$. Lyons (2) claimed that the red or purple color produced is not due to ferric thioglycollate but to the ferrothioglycollate ion, $Fe(SCH_2COO)_2^{=}$, in alkaline solution. Although the reaction is between ferrous iron and thioglycollic acid, both ferric and ferrous iron may be detected and estimated in the same solution as total iron.

The mechanism of the reaction between ionic iron and thioglycollic acid may be expressed as follows:

$$2Fe^{+++} + 2HSCH_2CooH \rightarrow 2Fe^{++} + \begin{matrix} SCH_2COOH \\ | \\ SCH_2COOH \end{matrix} + 2H^{+} \quad (1)$$

$$Fe^{++} + 2(SCH_2COOH)^{-} \rightarrow \underset{\text{Colorless}}{Fe(SCH_2COOH)_2} \rightarrow \underset{\text{Colored}}{Fe(SCH_2COO)_2^{=}} + 2H^{+} \quad (2)$$

Reaction (1) occurs only when Fe^{+++} is present. As soon as it is reduced, reaction (2) takes place, yielding the colored ion when a base is added. It is for this r reason that the total iron content of a solution may be determined. Strong bases and oxidizing agents discharge the color. Ammonia can be used to make the solution alkaline as it does not affect the intensity of the color quickly, even when present in large concentration.

Analytical Methods

These two methods have been tried in this laboratory to obtain this comparison and also to determine the iron content of some Alberta waters. Methods were those reported by Delaporte of Toronto, and by McCrady of Montreal to the Committee on Chemical Water Standards. Details of Delaporte's method were sent out June 1939, and McCrady's January 1940.

A. Delaporte's Method.

"Reagents: Solution of citric acid containing 20% wlv
Thioglycollic acid, reagent quality.
Solution of ammonia containing 10% wlwNH_3.
Standard iron solution.

The standard ferric iron solution is prepared by dissolving 0.7022 g. of crystallized ferrous ammonium sulfate in 50 ml. of distilled water, and 20 ml. of concentrated sulfuric acid. Warm the solution and add potassium permanganate solution until the iron is completely oxidized. Dilute to 1 liter, 1 ml. contains 0.1 mg Fe.

The color standards for the iron solution are prepared at the same time as the unknown.

We use the long form Nesslers, filling one to the 50 c.c. mark with the unknown, add 2 c.c. of 20% solution of citric acid and 0.1 c.c. of thioglycollic acid. Mix

and render alkaline with ammonia (about 2 c.c. of 10% ammonia) solution. After mixing, allow to stand for five minutes."

B. McCrady's Method

"To 5 c.c. of water sample (and to standards):

1. Add 1 drop concentrated HCl and mix well.
2. Place samples (not standards) in oven at 100°C for 15 minutes.
3. Remove from oven and allow to cool.
4. To samples (and standards) add 1 drop of thioglycollic acid and mix well.
5. Add 1 c.c. saturated sodium carbonate solution, and mix well.
6. Let stand 5 minutes and compare with standards.

This method permits detection of 0.1 ppm. of iron, which is ample for our routine work."

Using method A, standards were made up in Nessler tubes containing, 0.2,0.4,0.6,0.8,1.0,1.2,1.4,1.6,1.8, 2.0 ppm. of iron in 50 c.c. volumes. The water samples and the standards were made alkaline with 4 c.c. of the ammonia solution instead of 2 c.c. as suggested by Delāporte, as it was found that the color was more stable and for a longer period of time with this concentration of ammonia.

Using method B, standards were made up in flat bottomed test tubes, of approximately 10 c.c. capacity, containing 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.10 mg. of Fe diluted to 5 c.c.

C. Standard Method

This is the thiocyanate method as outlined in the Standard Methods of Water Analysis (1). This method was used to obtain a comparison for Methods A and B.

"Boil 50 ml. of the sample with 5 ml. 6N nitric acid for 5 minutes, add 3 drops of permanganate solution, and cool. Add 5 ml. of thiocyanate and compare immediately with standards prepared from the standard iron solution with 6N nitric acid."

Results and Discussion

It was first decided to try out method A in order to find whether ions ordinarily occurring in natural waters would have any effect. Solutions containing known amounts of iron and varying quantities of other ions were compared with standards containing only iron ions and distilled water.

Table I Effect of Various Ions - Method A.

Fe^{+++} Present PPM.	Fe^{+++} Found PPM.	Ca^{++} Present PPM.	Fe^{+++} Present PPM.	Fe^{+++} Found PPM.	$SO_4^{=}$ Present PPM.
1.0	1.0	50	1.0	1.0	123
1.2	1.2	100	1.2	1.3	246
1.4	1.4	150	1.4	1.6	369
			1.0	1.1	369
		Mg^{++}	1.2	1.2	492
1.0	1.0	30	1.0	1.1	615
1.2	1.2	60	1.2	1.2	738
1.4	1.4	90			
					$CO_3^{=}$
		$PO_4^{\equiv}$	1.0	1.0	90
1.0	1.0	79	1.2	1.3	180
1.4	1.5	237			
					HCO_3^{-}
		Zn^{++}	1.0	1.0	72
1.0	1.0	32	1.0	1.1	183
			1.2	1.2	366

The effect of Ca^{++}, Mg^{++}, $PO_4^{\equiv}$, Zn^{++}, $SO_4^{=}$, $CO_3^{=}$, HCO_3^{-}, ions in the range of concentrations that were used, appear to have no serious influence on the method for the determination of iron as shown in the above table. The effect of these ions were tried only on method A, since any ions affecting this method would probably affect method B in

the same way.

Table II - Comparison of Methods A,B, and C.

Lab. No.	A Fe PPM.	B Fe PPM.	C Fe PPM.
960	2.0	2.0	5.5
963	4.0	5.0	6.0
965	2.0	2.0	4.0
974	0.1	Trace	0.2
975	1.1	1.0	1.3
976	0.9	1.0	1.1
977	0.0	0.0	0.1
978	0.1	Trace	0.3
979	0.0	0.0	0.0
980	0.3	1.0	0.5
981	0.1	Trace	0.2

A number of natural waters were analyzed by the three methods for their iron content. Table II gives the results obtained with the three methods. The values with methods A and B are lower than the values with method C. This may be due to the fact that all of the iron has failed to go into solution, although no iron could be seen in suspension by the naked eye. Since the methods are accurate to -0.05p.p.m. of Fe, it can be seen that the three methods give results which are in the same range.

From the results in a report sent March 1940 by Bonham of the Department of Health of Ontario, it can be seen that his results with method A are lower than with method C. Some of Bonham's results are listed in the following table:

No.	Method A	Method C
1.	1.2	2.0
2.	None	0.05
3.	0.2	0.3
4.	0.04	0.1
7.	1.5	2.4
9.	0.4	1.0
11.	0.2	0.4
12.	1.7	2.0

It will be noted that his results with method A are lower than the results using the Standard Method.

In table III are listed the iron content of some Alberta waters. Delaporte's method (A) was used for the analysis of all of the waters and McCrady's method (B) for a few samples. It can be seen that up to 0.2 ppm. of Fe, the former method gives the higher results, and in most cases, above 0.2 ppm. of Fe the latter method gives the higher values.

Table III - Determination of Iron in Alberta Waters.

Lab. No.	A Fe PPM.	B Fe PPM.	Lab. No.	A Fe PPM.	B Fe PPM.
824	0.3		884	0.0	
808	0.1		887	0.5	
837	0.0		888	0.3	
866	0.1		889	0.0	
791	Trace		890	0.2	
793	0.1		891	0.0	
823	0.0		811	0.3	
832	0.1		919	0.9	1.0
783	0.1		920	0.3	1.0
839	0.2		921	0.0	
850	0.1		922	0.05	
865	0.8		923	1.5	
867	Trace		924	0.05	
904	Trace		925	1.4	1.5
912	Trace		926	0.05	
878	Trace		927	0.05	
879	0.4		928	0.7	1.0
880	0.0		929	0.0	
881	0.0		930	20.0	
883	0.1		931	0.0	

Lab. No.	A Fe PPM.	B Fe PPM.	Lab. No.	A Fe PPM.	B Fe PPM.
932	0.0		973	Trace	0.0
933-	0.3		974	0.1	Trace
934	0.0		975	1.1	1.0
935	1.6		976	0.9	1.0
936	0.0		977	0.0	0.0
937	0.1		978	0.1	Trace
938	1.6	2.0	979	0.0	0.0
939	0.0		980	0.3	1.0
940	0.05		981	0.1	Trace
941	0.0	0.0	982	0.3	
942	2.4	3.0	983	0.1	
943	0.0	0.0	985	Trace	
944	0.0		986	0.0	
945	0.0		987	0.0	
946	0.0		988	0.5	
947	0.0		989	0.1	
948	0.0		990	0.3	
949	0.7	1.0	991	0.3	
950	0.2	Trace	992	0.1	
951	0.2	Trace	993	0.3	
952	0.2	Trace	994	0.1	
953	0.0	0.0	995	2.0	
954	0.4	1.0	996	0.0	
955	0.8	1.0	997	0.1	
956	0.8	1.0	998	0.1	
957	0.1	0.0	999	1.6	
958	0.1	0.0	1000	0.9	
959	0.0	0.0	1001	0.2	
960	2.0	2.0	1002	0.1	
961	0.2	Trace	1003	?	
962	0.1	Trace	1004	0.0	
963	4.0	5.0	1005	0.0	
964	0.0	0.0	1006	0.0	
965	2.0	2.0	1007	0.0	
966	0.0	0.0	1008	0.0	
967	0.4	Trace	1009	0.3	
968	0.1	Trace	1010	0.9	
969	Trace	Trace	1011	0.0	
970	0.1	0.0	1012	0.0	
971	Trace	0.0	1013	0.1	
972	0.2	Trace	1014	0.1	

Comments

Using method A it was found more satisfactory to use 4 c.c. instead of 2 c.c. of the ammonia solution. With the smaller volume of ammonia, the color produced was found to fade in about one hour or less, while with the larger volume of ammonia the color of the solution persisted for a day or more.

High calcium concentrations in water cause the precipitation of carbonate as calcium carbonate when the saturated solution of sodium carbonate was added in method B. This effect was noticed for a large number of samples which were analyzed for iron with this method.

With the methods A and B, for concentrations up to 0.2 ppm. method A has given the higher values, and above 0.2 ppm. method B has given the higher values in the majority of cases.

Summary

The two methods proposed by the Committee on Chemical Water Standards have been described in full and comments on the methods have been made. The effect of various ions at varying concentrations have been shown and a comparison of the methods with the Standard Method is given. The values were found to be slightly lower.

The concentration of iron in Alberta waters varied from 0.0 to 5 ppm. with the exception of one sample which was found to contain 20 ppm. of Fe.

With this range of iron in waters, with the exception of the one sample, there is no serious effect on the titration method for sulfate determinations. Iron in the majority of water samples was present in the insoluble form, and was filtered off prior to the analysis of sulfates.

References

1. Standard Methods of Water Analysis, Ed. 8, 26, 73 (1936)
2. Lyons, E., Jour. Am. Chem. Soc., 49, 1916 (1927).
3. Andreasch, Ber., 12, 1391 (1879).
4. Claesson, Ber., 14, 411 (1881).

B29747